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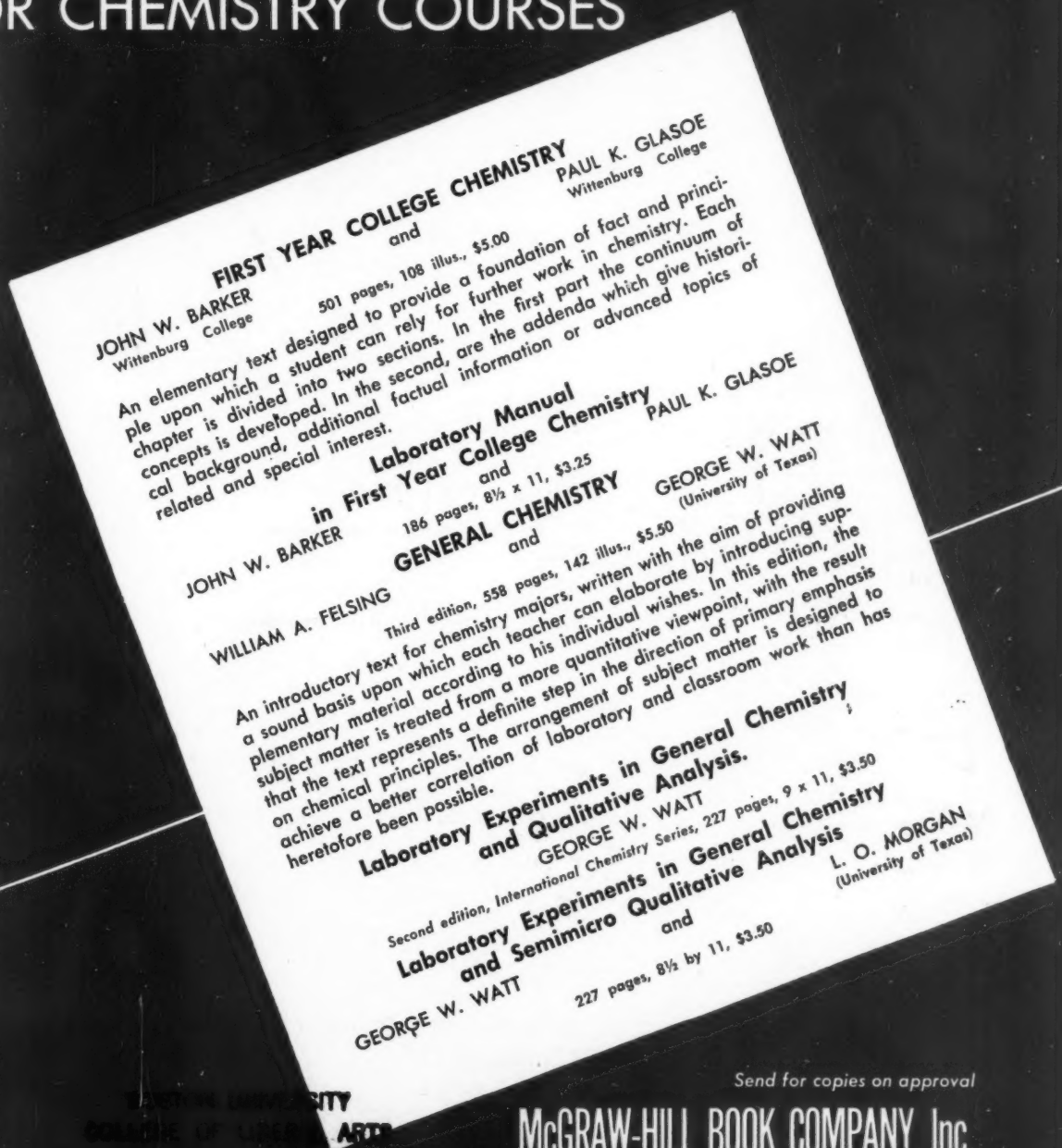
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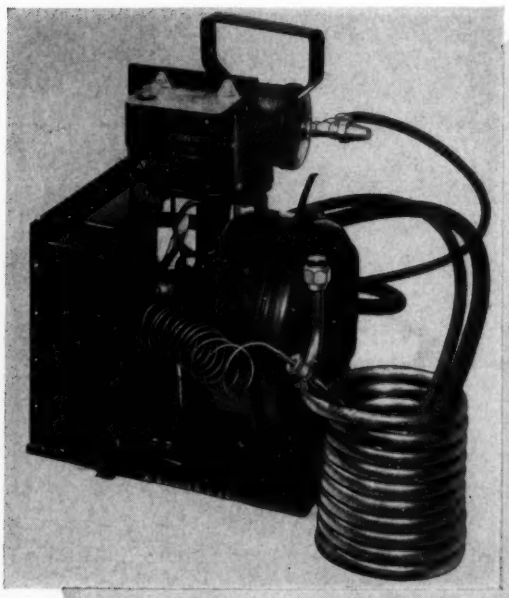

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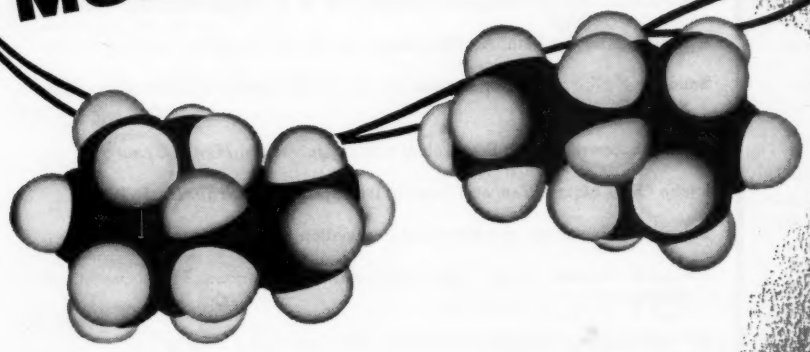

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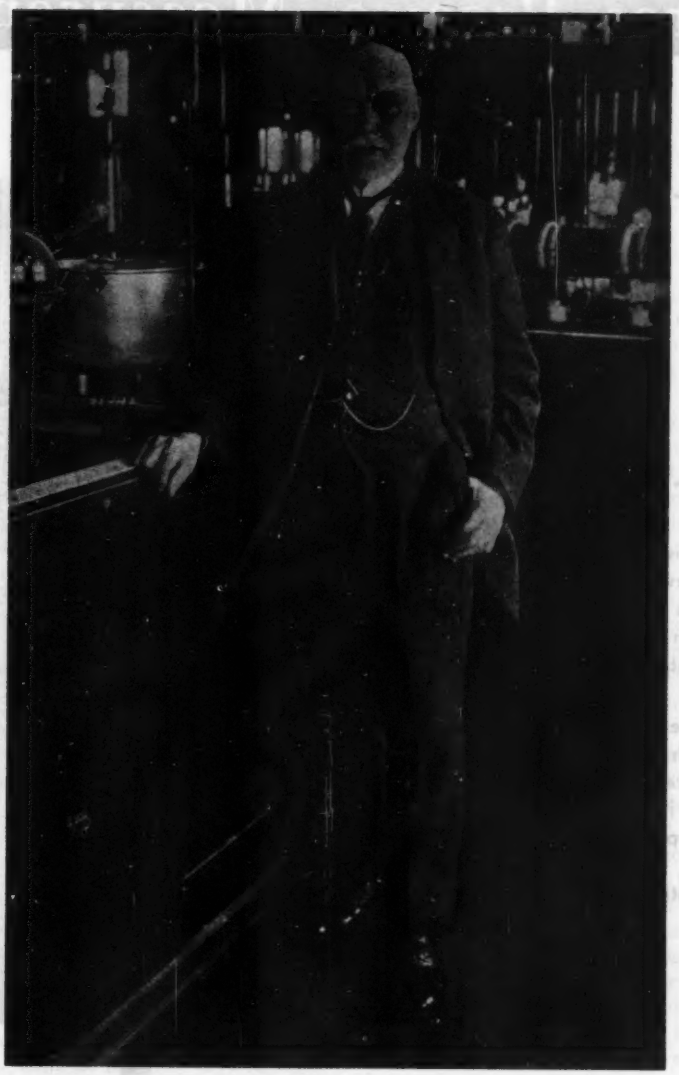

Frederick Belding Power, 1853-1927

(See page 258)

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Editor's Outlook

THE importance of education (or training—take your choice) is shown by the fact that agencies which were never in this field before are beginning to assume educational functions and responsibilities. Industry is of course the best example. Many progressive industries now regularly maintain training programs for their employees which often compare favorably with courses given in colleges and universities. Not only to equip their employees better for their jobs, but also to raise the general educational level, several large concerns have established programs of graduate and undergraduate scholarships. The educational value of summer jobs for undergraduates has been recognized to the point that such summer work is said to have been increased 300 per cent in the last few years, thus filling a need which has long been felt by technical schools, their students, and teachers.

All this is perhaps secondary to an even more important point: the dawning recognition by industry of its responsibility for helping to pay the rising costs of higher education. It gets too many golden eggs from this hen to allow the old bird to languish.

But another agency is coming into the picture. Institutions for both pure and applied research have multiplied during the last few decades. Some of these are attached to universities, but many of the largest are independent. Some of the large industrial research organizations belong in this category also, despite their industrial connections.

These research organizations are really exercising an educational function, whether or not it is recognized. Young men often come into these laboratories frankly to further their professional training, sometimes leaving for further academic work and degrees. The frequency with which academic posts are exchanged with research positions in these organizations shows their close connection with the recognized educational field. This relation will doubtless become closer and closer. When will we recognize it in a formal way?

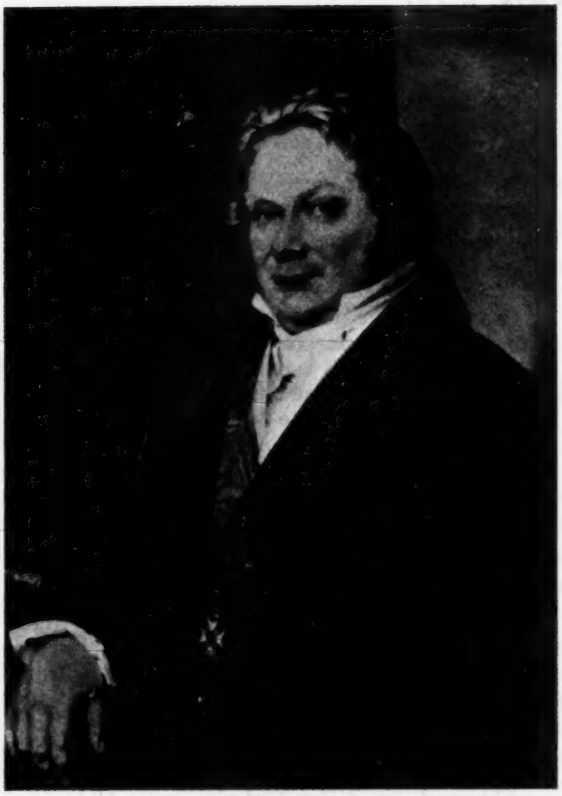
In a well-organized research organization a young man may go through as rigorous a course of training and development as his classmate who is working for a higher degree in the university. When this is true—and I have no doubt it is in some cases—it might well be acknowledged by some kind of permanent and visible stamp like the graduate degree. This mark, whatever it might be, would not be a substitute for the recognized academic degree, nor would it need to cheapen the latter. But many new elements and practices have come into the educational picture and change is so rapid that many more will appear. A proposal like this could be both useful and logical.

We are a long way from a stage of development in which any such plan could be administered. Agencies would probably have to be "accredited" by some competent professional organization. Busy industrial or research executives would perhaps insist that they could not afford such distractions nor undertake semi-academic responsibilities. But all sorts of people are now performing social functions which they never would have dreamed of a short time ago. All business men are now (perforce, and with not *too* much complaint!) doing the job of the tax assessor and making out their income tax returns regularly.

Of course, when a man has served a term in a research laboratory the fact goes into his personnel record and a future employer can find it if he is interested. So frequently the specifications read: "The Ph.D. or the equivalent." Well, here is a way in which we might start to regularize the equivalent. As things stand now, the man who has "the equivalent" has to dig it out of the papers—if he can find it—while his classmate writes *his* equivalent with his name. To be sure, this is one of the facts of life—but *some* of the facts of life could perhaps be changed.

FARADAY'S ELECTROCHEMICAL LAWS AND THE DETERMINATION OF EQUIVALENT WEIGHTS[1]

ROSEMARY GENE EHL and AARON J. IHDE
University of Wisconsin, Madison, Wisconsin



Jöns Jakob Berzelius

As soon as the atomic theory was announced by Dalton it became apparent to those who accepted atoms as the fundamental units of matter that the determination of relative atomic weights was an activity of primary importance. The well-meant but pitifully inaccurate analyses made by Dalton produced the first table of relative atomic weights. There were others who made analyses, but it was Berzelius who shouldered the burden of making systematic determinations of atomic weights of the known elements. Before atomic weights could be assigned, however, it was essential that combining or equivalent weights be determined as accurately as possible, and it is here that the great experimental genius of Berzelius is especially well illustrated. He devoted ten years of his life to the determination of over 2000 combining weights of elements. With relatively crude balances, impure chemicals, and very little equipment at his disposal, Berzelius labored at this gigantic task under conditions which most present-day chemists would describe as completely unbearable. Yet his results were excellent and his equivalent weights are not far removed from modern values.

During his lifetime a uniquely simple and accurate method of determining equivalent weights became available to Berzelius. In January, 1834, Michael Faraday announced the discovery of the electrochemical laws. Subsequent researches led him to the investigation of the electrochemical equivalents of several elements and finally to the conclusion that the electrochemical equivalents are identical with the ordinary chemical equivalents. Here was a method devoid of the endless and tedious precipitations, filtrations and weighings of the purely chemical procedures used by Berzelius. Here, too, was a method supported by what proved to be one of the most accurate laws known to science.

It is strange that Berzelius did not grasp at this approach, if not to replace his chemical methods, at least to provide a check on them. He was not unfamiliar with electrochemical manipulations, for he was an expert in the field, having begun his brilliant scientific career with investigations on the effects of the voltaic pile soon after its development in 1800. Yet there is only one shred of evidence that Berzelius ever determined chemical equivalents by use of the method outlined by Faraday, and even this evidence is questionable (see footnote 26). On the other hand, there is considerable evidence that Berzelius chose to neglect this discovery by the greatest scientist in England.

Although the "law of definite electrochemical action," as he named it, was not formally announced by Faraday until January, 1834, the notion that chemical effects in electrolysis are dependent on the quantity of electricity passed seems to have occurred to him much earlier. In his third series of researches published in January, 1833, Faraday remarked:[2]

> When electrochemical decomposition takes place, there is great reason to believe that the quantity of matter decomposed is not proportionate to the intensity, but to the quantity of electricity passed.

[1] Presented before the Division of the History of Chemistry at the 124th Meeting of the American Chemical Society, Chicago, September, 1953.

[2] *Trans. Roy. Soc. London*, 123, 39 (1833).

Faraday took great pains to distinguish between quantity and intensity of the electric current. He used the words carefully and correctly and was seemingly well aware of the distinguishing characteristics and effects of each. This is a matter of no small importance, for it was precisely confusion on this point which helped to lead Berzelius astray.

The seventh series of researches published in January, 1834, is devoted to the work on electrochemistry and represents the final report of work which was referred to months earlier. Faraday found the prevailing electrochemical nomenclature unnecessarily confusing and proposed the use of the term "electrode" in place of "pole." He also suggested use of the terms anode, cathode, electrolyte, electrolyze, ion, cation, and anion.[3] Faraday first tested the law of definite electrolytic action on water under a variety of conditions.[4] When investigating the effect of variation in the size of electrodes, variation in current intensity, and variation in the concentration of the sulfuric acid solution used, he found that none of these three factors affected the amount of chemical action if the quantity of electricity remained the same. He also found that the law of definite electrochemical action was valid for aqueous solutions other than those of sulfuric acid. Faraday stated his final conclusions thus:[5]

...that when subjected to the influence of the electric current, a quantity of it (water) is decomposed exactly proportionate to the quantity of electricity which has passed...

These first experiments were all performed as preliminary steps in justifying the use of a current-measuring instrument which Faraday had invented and called a "volta-electrometer." The name was changed to "voltameter" in 1838 and then to "coulometer" about 1902. Faraday's instrument consisted of two graduated glass tubes provided with electrodes and containing acidulated water. Mixed hydrogen and oxygen or the hydrogen alone was collected, the amount of gas collected giving a measure of the current which had passed. Faraday planned on using this device rather extensively in his future work in electrochemistry.

Upon considering the law of definite electrochemical action fully proved for the electrolysis of water, Faraday proceeded to apply it to other substances. He electrolyzed the fused protochloride of tin ($SnCl_2$) and by means of the gas volume in the volta-electrometer determined the electrochemical equivalent. The average of four experiments gave 58.53 as the value for the equivalent as compared with 57.9 which was quoted as the chemical equivalent. Faraday could not but conclude:[6]

...that the numbers leave little doubt of the applicability of the law of *definite action* in this and all similar cases of electrocomposition....

[3] *Ibid.*, 124, 77–9 (1834).
[4] *Ibid.*, pp. 87–91.
[5] *Ibid.*, p. 91.
[6] *Ibid.*, p. 104.

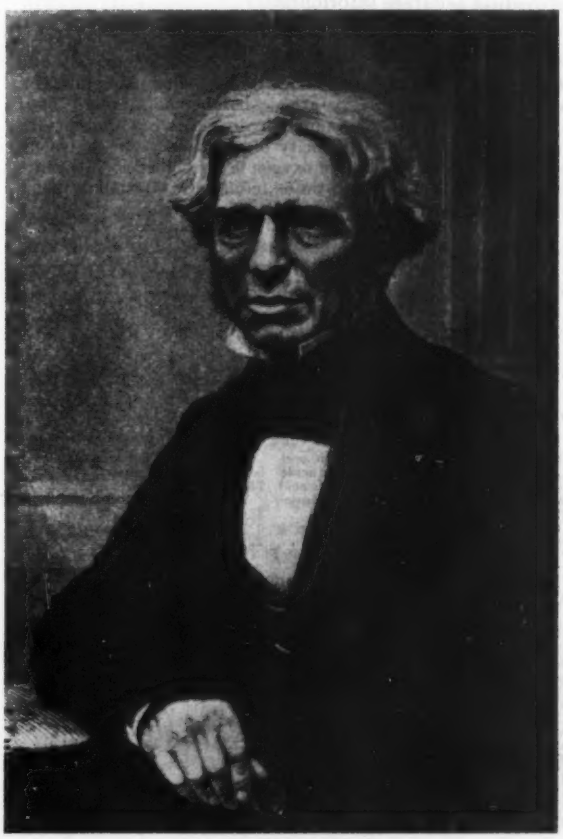
It is not often I have obtained an accordance in numbers so near as that I have just quoted.

Faraday electrolyzed many other substances, among them the chloride of lead, for which he again obtained results approximately equal to the chemical equivalent. To further establish the validity of the electrochemical law, Faraday resorted to using electrodes of different substances as well as using arrangements in which the metal under investigation was employed as the positive electrode so that there would be a direct transfer of metal from one electrode to the other. From these latter experiments Faraday happily found that the positive electrode lost as much weight as the negative electrode gained and all in equivalent proportion to the water decomposed in the voltameter.[7]

All these facts combine into, I think, an irresistible mass of evidence, proving the truth of the important proposition which I at first laid down, *namely, that the chemical power of a current of electricity is in direct proportion to the absolute quantity of electricity which passes.* They prove, too, that this is not merely true with one substance, as water, but generally with all electrolytic bodies....

That Faraday considered the electrochemical equiva-

[7] *Ibid.*, p. 110.



Michael Faraday

lents and the chemical equivalents as identical is brought out by the following remarks in his paper:[8]

> After the first experimental investigation to establish the definite chemical action of electricity, I have not hesitated to apply the more strict results of chemical analysis to correct the numbers obtained as electrolytic results....
>
> The equivalent numbers do not profess to be exact, and are taken almost entirely from the chemical results of other philosophers in whom I could repose more confidence, as to these points, than in myself.

At this point Faraday inserted a "Table of Ions" which might more properly be considered a table of equivalents. It is of interest to note the method by which Faraday arrived at this table. What he apparently did was to determine the electrochemical equivalents for a number of substances by electrolytic methods. These results were then used to give an idea of the magnitude of the value, and then the chemical equivalents taken from other sources (probably Berzelius) were adjusted to fit this value. The values for tin and lead, for instance, are not those which Faraday had found by experiment, but are the chemical equivalents which his electrochemical results had closely approximated. The table itself gives the impression of being rather hastily put together, with the idea, as Faraday indicated, of showing the way rather than of providing accurate information.

Faraday was careful to point out that:[9]

> A very valuable use of electrochemical equivalents will be to decide, in cases of doubt, what is the true chemical equivalent, or definite proportional, or atomic number of a body.... I can have no doubt that, assuming hydrogen as 1, and dismissing small fractions for the simplicity of expression, the equivalent number or atomic weight[10] of oxygen is 8, of chlorine 36, of bromine 78.4, of lead 103.5, of tin 59, etc., notwithstanding that a very high authority doubles several of these numbers.

While no names are mentioned, the "high authority" undoubtedly refers to Berzelius. Berzelius considered the true equivalent of hydrogen to be a double atom, H_2, and considered this equivalent to K, Zn, etc. Thus he was inclined to write KO, AgO, KCl_2, $NaSO_4$, etc. and the atomic weights of potassium, sodium, lithium, and silver were doubled. Faraday showed how the electrochemical equivalents could be used to decide matters of this kind, for the table which he offered is essentially correct as regards equivalents.

Faraday's position is clear. He discovered the laws of electrochemistry and suggested methods for their use, but this was as far as he cared to take the problem. Further work on equivalents would have led him into the field of atomic weight determinations and Faraday had not yet convinced himself of the existence of atoms. Faraday, the experimental genius, like many great experimenters, was not fond of theories or speculation in any form. Rather, he chose to trust the concrete facts which he could collect as a result of researches in his laboratory. In this respect he was like his teacher, Davy, from whom he perhaps acquired much of his dislike of theoretical speculation.

In the very same paper in which he announced the electrochemical laws he showed his distaste for the atomic theory by making the following statement:[11]

> ...but I must confess I am jealous of the term *atom;* for though it is very easy to talk of atoms, it is very difficult to form a clear idea of their nature, especially when compound bodies are under consideration.

The reluctance to carry the study of equivalents further than he had already done was no doubt a result, at least in part, of this aversion to the particulate theory of matter.

Other people were, at this time, substantiating the validity of the electrochemical laws. In a letter to Faraday, John Frederic Daniell, inventor of the Daniell constant cell and obviously a great admirer of Faraday, had remarked:[12]

> One result, I know will gratify you; namely, that amongst the almost innumerable tests to which I have exposed your great discovery of the *definite chemical action of electricity,* I have found no fact to militate against it....

In Italy the electrochemical laws apparently underwent an independent discovery soon after Faraday had announced them. The discoverer was Carlo Matteucci, a man of whom little is written in the English language, and who is seemingly almost unknown to the historians of science, although in 1848 he received the Copley medal in London and is considered the originator of modern electrophysiology.

Matteucci, chemist, physiologist, and physicist was born at Forlì in 1811 and died at Ardenza, near Leghorn, in 1868. He received his doctor's degree in mathematics at the University of Bologna in 1828 and then continued his studies in Paris, where he had the opportunity to meet the great men who associated

847. TABLE OF IONS.

Anions

Oxygen	8	Selenic acid	64	Tartaric acid	66
Chlorine	35·5	Nitric acid	54	Citric acid	58
Iodine	126	Chloric acid	75·5	Oxalic acid	36
Bromine	78·3	Phosphoric acid	35·7	Sulphur (?)	16
Fluorine	18·7	Carbonic acid	22	Selenium (?)	
Cyanogen	26	Boracic acid	24	Sulpho-cyanogen	
Sulphuric acid	40	Acetic acid	51		

Cations.

Hydrogen	1	Cadmium	55·8	Soda	31·3
Potassium	39·2	Cerium	46	Lithia	18
Sodium	23·3	Cobalt	29·5	Baryta	76·7
Lithium	10	Nickel	29·5	Strontia	51·8
Barium	68·7	Antimony	64·6?	Lime	28
Strontium	43·8	Bismuth	71	Magnesia	20·7
Calcium	20·5	Mercury	200	Alumina	(?)
Magnesium	12·7	Silver	108	Protoxides generally	
Manganese	27·7	Platina	98·6?	Quinia	171·6
Zinc	32·5	Gold	(?)	Cinchona	160
Tin	57·9			Morphia	290
Lead	103·5	Ammonia	17	Vegeto-alkalies generally.	
Iron	28	Potassa	47·2		
Copper	31·6				

Faraday's Table of Equivalents

[8] *Ibid.*, p. 114.
[9] *Ibid.*, pp. 115–16.
[10] Note Faraday's misuse of the term "atomic weight."
[11] *Trans. Roy. Soc. London,* **124**, 121 (1834).
[12] *Ibid.*, **126**, 107 (1836).

themselves with Arago. Although he was mainly interested in electrophysiology, he conducted researches in many other fields of science.[13, 14]

It was after his return from Paris in 1831 that he continued, in Forlì, the research he had started in Forlì on the action of electric current upon chemical combination. The short biography in the "Enciclopedia Italiana" makes this statement:

> As a result, he was able to demonstrate the law of proportionality between the quantity of deposited electrolyte and the quantity of electricity passed through the voltameter, and this he did independently of the well known experiments by Faraday. Furthermore, he was able to draw conclusions of such an importance that Faraday himself said that they had given the young Italian scientist—at that time in his early twenties—a European fame.

Matteucci's paper containing the work on the law of definite electrochemical action bears the date October, 1834, and is published in the French *Annales* for January, 1835.[15] Matteucci measured the quantity of current by using a silver coulometer. With this instrument in the circuit he conducted experiments in which zinc was destroyed with acid. Despite conditions in which he varied the concentration of acid, the temperature, and the surface area of the zinc, he always obtained the same current from the same weight of metal. Through other experiments Matteucci came to two additional conclusions:[16]

> *In causing the electric current developed by a certain chemical action to pass through different metallic solutions, the quantities of metals reduced and separated in these different solutions are variable, and whatever may be their relative densities, they are always in the same ratio as the chemical equivalents of these same metals.*
>
> There is finally the third and last result at which I have arrived, and which can well be regarded as the necessary consequence of the other two: *in disposing of different metals in the form of a pile, so that their decomposed quantities are in the same ratio as their chemical equivalents, one obtains a uniform electrochemical action.*

Matteucci seems to have arrived at the same conclusions as Faraday. The question of whether the discovery was independent is an interesting one. The "Enciclopedia Italiana" says that it was, but this source might be expected to favor Matteucci's position.

In the *Annales* for 1839,[17] Matteucci published another article in which he commented on his previous discovery. In this comment he claimed independent discovery of the electrochemical laws but gave Faraday credit for the original discovery and for the establishment of the law of definite electrochemical action. This notion apparently did not prevail among certain other European scientists. In the *Philosophical Magazine* Poggendorff affirmed Faraday's priority to the discovery of definite electrolytic action.[18] Poggendorff felt that Faraday had been greatly wronged. He admitted that since news traveled slowly to Italy Matteucci might not have known of Faraday's discovery. However, Poggendorff felt that Gay-Lussac and Arago, editors of the *Annales*, surely were aware of Faraday's discovery and therefore should not have published Matteucci's article in the form in which it appeared.

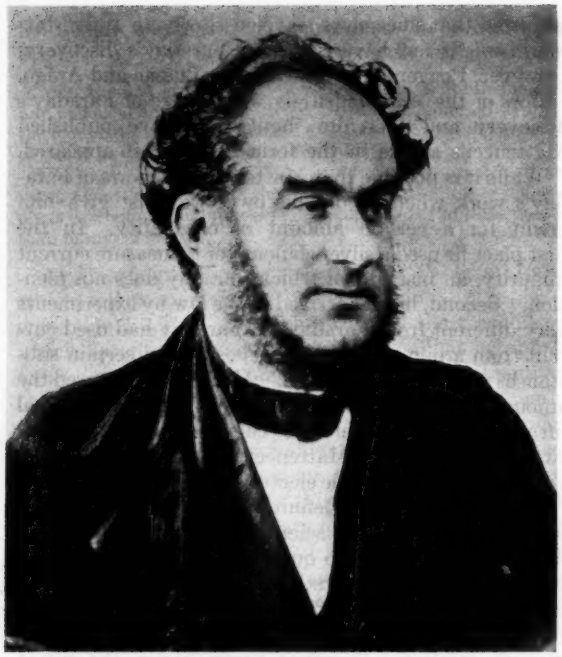
While it is possible that Matteucci was aware of Faraday's work when he did his own, we must give him credit for a certain amount of originality. In the first place he used a silver coulometer to measure current quantity, an instrument which Faraday does not mention. Second, he had arrived at the law by experiments very different from Faraday's. Faraday had used current from a pile to cause the deposition of certain substances which he could weigh. Matteucci measured the amount of current which a known amount of metal furnished as it underwent chemical action. These two facts strengthen Matteucci's position as the independent discoverer of the electrochemical laws.

While the law of definite electrochemical action was accepted by many scientists as a well established fact, there was one who questioned its validity. This was Berzelius, who first learned of Faraday's discovery from Poggendorff's *Annalen*,[19] in which Faraday's seventh series of researches was reprinted in complete translation. Berzelius' comments on the law of definite electrochemical action made their appearance in the 1836[20] volume of his *Jahres-Bericht*. These comments begin with a brief summary of the conclusions which Faraday had drawn from his experiments. Berzelius registers his first complaint against the conclusion that the concentration of sulfuric acid had no effect on the amount of hydrogen and oxygen evolved during the electrolysis of water if the current quantity remained the same:

> Hereby, however, it seems to me that an error of observation could have been made. With the passage of the electric current through the acidic liquid, acid collects in excess amount at the positive pole and water at the negative pole, and the amount must vary with the unequal amount of the acid. But if a fixed quantity of electricity is used for this division with water and concentrated acid, then, so it seems, variations must take place in the quantity of water which is decomposed into its constituents. Even if the sum of both decompositions is the same each time, then surely both types can vary among themselves in relative quantity.

Considering Faraday's reputation as an experimenter, the suggestion that Faraday had made an error in observation was a bold step. Berzelius, however, was not one to hesitate! The fallacy in Berzelius' argument results from his failure to see that the *quantity* of electricity is related only to those substances actually separated at the electrode even though it is true that acid does collect around the anode. The irregularities which Faraday did find he attributed to solubility

[13] "Enciclopedia Italiana," Rome, 1934, p. 596.
[14] BIANCHI, N., "Carlo Matteucci e l'Italia del suo tempo," Turin, 1874. The portrait is taken from this work.
[15] *Ann. chim. et phys.*, **58**, 75 (1835).
[16] *Ibid.*, pp. 78–80.
[17] *Ibid.*, **71**, 90 (1839).
[18] *Phil. Mag.*, [3] **7**, 421–2 (1835).
[19] *Ann. Phys. Chem.*, **33**, 301, 433, 481 (1834).
[20] *Jahres-Bericht*, **15**, 30–9 (1836). The two-year lag in the material published in the *Jahres-Bericht* was not unusual since Berzelius was outside the main center of scientific activity in Europe. The Berzelius quotations which follow are all translations from this reference. The translations are the authors'.



Carlo Matteucci

effects of the gases and not to the failure of the law of definite electrolytic action. Berzelius continues his comments and objections:

He declares further to have found that the same number of couples in the pile, charged stronger or weaker (what is to be understood by this is not indicated for certain. It would be entirely wrong, however, if it meant "built up with fluids of unequal electromotive force"), gave the same quantity of hydrogen gas, and also showed the same ratio, when at one time the pile consisted of 5 couples and at another time consisted of 10 couples, provided plates of the same size had been used.

Here we see that Berzelius has hopelessly confused the concepts of current quantity and current intensity. He cannot see that "strongly and weakly charged" and the number of couples in the pile refer to variations in current intensity which need not affect the current quantity, on which chemical effects are dependent.

Berzelius continues with a statement of Faraday's conclusions on the decomposition of water and the use of the volta-electrometer as a current measure. Then he comments on the electrochemical equivalents:

In this way Faraday comes to the third and principal result of his experiments, namely "*that those things which the same quantity of electricity decomposes are chemical equivalents.*" The proofs for this principle are not many, to be sure. They surely seem, however, to show this behavior for the cases mentioned. Thus he found that with hydrochloric acid and hydriodic acid dissolved in water each gave the same quantity of hydrogen gas at the negative pole which he had obtained in the quantity measured with dilute sulfuric acid.... When silver chloride, and especially lead chloride in molten condition, was decomposed between platinum wires, of which the negative was weighed, then it became apparent that the weight of the reduced metal adhering to the negative wire corresponded to the volume of the hydrogen gas collected in the quantity measured, in such a manner, that both were chemical equivalents....

In the evaluation of these experiments it appears as if the theorem stating that the same quantity of electricity always gives the same amount in decomposition has not been proved as completely as one could wish. The fact is perhaps correct. This must not keep us from a closer criticism of the proof.

The skepticism of Berzelius is quite evident at this point but he has some other more important objections:

In the results of these experiments I find nothing that would be decisive enough to prove more than that if water and melted lead chloride[21] are decomposed one after the other by the same electric current the quantities of the reduced lead and hydrogen are equivalents. But also here the presence of sulfuric acid[22] in the water causes an uncertainty, as I mentioned before. It must cause a variation, which is perhaps too small to show up, when the experiment must be carried out on such a small scale. Still another question can be asked here: is the same quantity of electricity necessary to separate one atom of silver and one atom of oxygen from each other, as to separate one atom of potassium from one atom of oxygen,[23] that is, to neutralize forces of such an immense difference in magnitude? Can the intensity in strength compensate, as it is to be assumed, for the overcoming of a great force? Would not the condition be conceivable that affinities of the same amount are equally overcome by the same current and affinities of a little different degree with such a small difference in their amounts that in a small-scale experiment it falls into the errors of observation? It is known that lead separates chlorine from hydrogen only with difficulty and on boiling and that therefore these affinities lie very close. One sees from this that this investigation must be taken from a much broader viewpoint, before the result which Faraday has inferred from it can be considered as valid.

That Berzelius is confusing the roles of current intensity and current quantity is evident, for he suggests that it would take more *current* to separate the atoms in a stable compound than in a less stable one. It also happens, says Berzelius, that lead and hydrogen possess about the same combining tendency or affinity for chlorine, since it is hard for lead to replace hydrogen in hydrochloric acid. Hence it ought to take almost the same *current* to separate lead from chlorine as hydrogen from oxygen and this then explains why Faraday gets consistent results, with the provision, of course, that there be a difference in the current quantity, but this is so small in this instance that Faraday has missed it.

There is at least one respect in which Faraday's work can be genuinely criticized. Faraday was under the false impression that only compounds composed of single equivalents of each element could be decomposed by the electric current. He was led to this hypothesis as a result of testing various substances for conductivity and decomposition. He found, for instance, that $SnCl_2$ was decomposed but $SnCl_4$ was not. If substances which were known not to consist of single equivalents were decomposed, Faraday thought this

[21] Of all Faraday's experiments, Berzelius seems to be most favorably impressed with the results obtained with lead chloride.

[22] That is, the acid used to make the water in the volta-electrometer conducting.

[23] Note the Berzelian formulas AgO and KO.

was the result of some secondary action at the electrodes and was not the primary decomposition caused by the electric current. Ammonia was one of these substances. When Faraday attempted to decompose Sb_2O_3 and $SbCl_3$ he found that he got decomposition although he knew these substances did not consist of single equivalents. He was so convinced of the correctness of his single equivalent theory, however, that he proposed the existence of an oxide and a chloride of antimony containing the proportions of 1:1 which had up to this time been unknown. These alleged compounds were assumed to be present in the ordinary antimony compounds and were responsible for the conducting power of these compounds. By some experiments which he himself described as rough, he thought he had prepared the true antimony compounds SbCl and SbO. His experiments were done hastily and were, from an analytical point of view, rather incomplete.

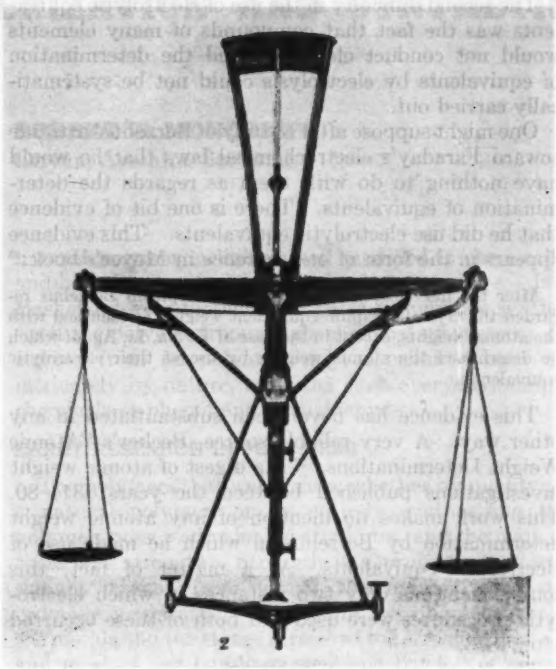
Berzelius objected to these new compounds described by Faraday and repeated Faraday's experiments more carefully. He found Faraday to be completely mistaken regarding the existence of the new compounds. Faraday later admitted his error in regard to the antimony compounds but he did not offer to retract his theory on single equivalents or the electrochemical laws, both of which he still believed to be correct.

Berzelius concludes his remarks with a rather violent attack upon Faraday's new electrochemical nomenclature:

> Faraday believes, for reasons which I do not consider valid, that his experiments lead to such changed views in the theory of science that our usual scientific nomenclature is inadequate for a correct expression of the ideas to which the results lead; therefore he has introduced others of which I do not think either that they were necessary in any respect, or that they deserve to be followed....
>
> It is obvious to everyone that a new nomenclature established on the idea of only one electricity has never been more superfluous than in the moment when the electrochemical theory,[24] which without two opposite electrical forces would make no sense, is on the way to winning such strong support, as from the electrical quantitative relations which Faraday has sought to establish.

One must conclude from Berzelius' remarks that he was not convinced of the correctness of the law of definite electrochemical action. To the extent that Faraday's work supports his own electrochemical theory he is willing to accept Faraday's results. It is quite obvious, however, that he does not approve at all of the electrochemical nomenclature introduced by Faraday.

A word must be said about the confusion concerning the meaning of the words "equivalent weight" and "atomic weight." Among the chemists of this period the definitions for these terms were a matter of personal preference and no one agreed on the meaning of "equivalent," "atom," or "atomic weight." The word "molecule" was literally unknown, having been rejected along with Avogadro's hypothesis about 1811. "Atom" or "compound atom" was often used where "molecule" was meant. Some used equivalent and atomic weight synonymously. Even Faraday himself had done this. Berzelius seems to have been one of the few who had a clear concept of the difference between an equivalent weight and an atomic weight. The trouble over equivalents arose, however, not so much over incorrect ideas as over the multiplicity of points of view and lack of a generally accepted standard. The electrolytic equivalents could have been used most effectively as a standard but the idea was not consistently carried out.



A Berzelius Balance

Lothar Meyer, in his "Outlines of Theoretical Chemistry,"[25] mentions that there were two main difficulties in determining equivalent (not atomic) weights by use of Faraday's law. One of these was the fact that several metals such as copper displayed different values for their equivalents, depending on the nature of the compound investigated. The problem of which equivalent to select as the true equivalent which the symbol would represent was one which beset almost every chemist of the period. Some elements had only two equivalents but there were others, manganese, for instance, that had six equivalents. The smallest one was often used as the true equivalent. Faraday had been troubled by this too. He believed that there could be only one electrolytic equivalent for an element.

[24] This refers to Berzelius' own electrochemical or dualistic theory which explained chemical combination and electrodecomposition on the basis of two oppositely charged forces.

[25] MEYER, L., "Outlines of Theoretical Chemistry," Longmans, Green and Co., London, 1892, pp. 16–17 (1st German edition, 1890).

The second difficulty in the use of electrolytic equivalents was the fact that compounds of many elements would not conduct electricity and the determination of equivalents by electrolysis could not be systematically carried out.

One might suppose after a study of Berzelius' attitude toward Faraday's electrochemical laws that he would have nothing to do with them as regards the determination of equivalents. There is one bit of evidence that he did use electrolytic equivalents. This evidence appears in the form of one sentence in Meyer's book:[26]

> After the discovery of the law of isomorphism Berzelius regarded the crystallographic equivalent weights as identical with the atomic weights, except in the case of K, Na, Li, Ag, of which he determined the atomic weights by use of their electrolytic equivalents.

This evidence has never been substantiated in any other way. A very reliable source, Becker's "Atomic Weight Determinations,"[27] is a digest of atomic weight investigations published between the years 1814–80. This work makes no mention of any atomic weight determination by Berzelius in which he made use of electrolytic equivalents. As a matter of fact, this source mentions only two instances in which electrolytic procedures were used and both of these occurred after 1873.

The most important point which emerges at this time is the fact that the electrochemical laws of Faraday were almost completely neglected between 1834 and 1880. Some recognized them as a great discovery but the almost immediate opposition on the part of Berzelius dealt a telling blow to their complete acceptance. Berzelius, the "law-giver of chemistry" and the undeniable "first authority" in chemical matters, had to give his stamp of approval before a matter as important as this could be said to be accepted. This approval was unquestionably lacking and may be said to be the most important single factor in the neglect of Faraday's laws.

Berzelius apparently maintained this opposition to the end of his life.[28] In the fifth edition of his "Lehrbuch der Chemie"[29] he mentions the laws and seems even more convinced of their incorrectness:[30]

> It is absolutely too early, indeed only conjectural, to accept the admission of these results for a general valid natural law... there occurs no comparison between the quantity of that which is separated in unlike substances and the quantity of the current.

As far as Faraday's theory of single equivalents and secondary action was concerned, Berzelius classified them as "...conclusions which require only a small application of logic in order to be rejected."[31]

Besides the objections of Berzelius there were some other factors which accounted for the neglect of the electrochemical laws. Faraday's own distrust of the atomic theory and his reluctance to carry his work on equivalents beyond the publication of his "Table of Ions" were undoubtedly contributing factors. His false interpretations of certain parts of his work, especially on the theory of single equivalents, certainly hurt his position, since the law of definite electrochemical action was intimately connected with this false hypothesis. The confusion over the meaning of "equivalent" and the existence of several equivalents for one element, as well as the fact that not all substances could be electrolyzed to give their electrochemical equivalents, were of importance also.

With all these factors operating toward the defeat of Faraday's electrochemical laws it is not surprising that as late as 1900 Louis Kahlenberg[32] and T. W. Richards and his associates[33] were conducting studies to determine whether Faraday's law was universally applicable and valid under such simple conditions as, for example, for nonaqueous solutions and at different temperatures.

[26] *Ibid.*, p. 20.

[27] BECKER, G. F., "The Constants of Nature. IV: Atomic Weight Determinations," Smithsonian Misc. Coll. 358 (1880).

[28] Berzelius died in 1848.

[29] BERZELIUS, J., "Lehrbuch der Chemie," 5th ed., Arnoldische Buchhandlung, Leipzig, 1856, pp. 99–101. (Forward to the book bears the date 1842.)

[30] *Op. cit.*, pp. 100–1.

[31] *Ibid.*

[32] *J. Phys. Chem.*, 4, 349 (1900).

[33] *Proc. Am. Acad. Arts Sci.*, 38, 409–13 (1902).

CHEMISTRY INSTITUTE

THE program has been announced for the First Chemistry Institute for college chemistry teachers, to be held July 19 to August 20 at Laramie, Wyoming. The Institute is being sponsored by the A. C. S. Division of Chemical Education, the National Science Foundation, and the University of Wyoming.

Mornings will be devoted to Recent Advances in Chemistry and Their Application in Undergraduate College Teaching. The lecturers and discussion leaders will be John C. Bailar, Jr., Farrington Daniels, Philip J. Elving, George Gamow, Joel H. Hildebrand, Willard F. Libby, Glenn T. Seaborg, Ernest H. Swift, and Gerrit Van Zyl.

Afternoons will include lectures on various subjects by Hubert Alyea, Alfred B. Garrett, Harrison Hale, Harry C. Kelly, Walter Kirner, Norris W. Rakestraw, Otto M. Smith, B. R. Stanerson, Calvin VanderWerf, and others. Much of the afternoon time will be left free for discussion of whatever topics are desired by groups of registrants. Possibilities include: challenging the superior student; content of chemistry courses of majors and nonmajors; laboratory experiments; lecture demonstrations; chemistry in general education; physical science courses; correlation of high-school and college chemistry; recruitment of chemists, etc.

Evenings and week-ends will in general be left free for recreation or study.

Expenses of 20 to 30 registrants will be paid by a fund from the National Science Foundation.

Directors of the Institute are William E. Morrell, University of Illinois, and E. R. Schierz, University of Wyoming. Requests for further information, and applications for enrollment or for expense grants should be sent to Professor Schierz at Laramie.

LINEAR POLYMERIZATION AND SYNTHETIC FIBERS

ROBERT W. MONCRIEFF
Girvan, Ayrshire, Scotland

Most of the materials that we encounter in everyday life are polymers: wood, rubber, plastics, paper, wool, cotton, rayon. For a long time the chemistry of polymers was not understood, and it was thought that their constitution was variable and unorganized. When natural polymers were analyzed by classical methods, the results, although showing some rough sort of uniformity, were not exactly consistent. It was well known that when a simple nonpolymeric substance such as silver chloride was analyzed the results were always exactly consistent, and it was indeed on this accuracy of repeat that the fundamental laws of chemical combination had been based.

The chemist, accustomed to analyzing silver chloride and finding in it a constant proportion of chlorine, was baffled when he analyzed wool and found that sometimes it contained one per cent of sulfur and sometimes as much as three per cent, while other samples could have any values intermediate between these two extremes. He soon realized that attempts to describe the constitution of wool in terms of the conventional formula $C_xH_yO_zN_aS_b$ were unprofitable, and he shelved analytical work on wool and similar materials in favor of work on simple chemical substances such as benzene, camphor, and cocaine which, while possessing very different degrees of molecular complexity, did at least have in common the virtue of constancy of composition. One sample of camphor always contained just as much carbon, just as much hydrogen and just as much oxygen as another. Such materials were tractable and the methods of classical analysis could be applied to them to give immediately their empirical formulas and after further research their constitutional formulas.

But although polymers proved to be very difficult subjects for the chemist, and particularly for the academic chemist, the industrialist was not slow to see in the polymers materials which had very interesting properties and great possibilities. It did not really matter that he had no proper appreciation of the chemistry of cellulose, if nevertheless he was able to nitrate it, plasticize the product of nitration with camphor, and arrive at a quite new product, celluloid, which had new and fascinating properties.

The lack of understanding of the chemical processes involved in the reaction between phenol and formaldehyde did not deter Baekeland from making Bakelite, probably the first true synthetic plastic, the first plastic material to be derived entirely from simple chemical entities. The industrialists who had made celluloid had not made the *polymer;* they had rather started with a natural polymer, cellulose, had modified it chemically and had thereby modified its physical properties. But Baekeland went further than this; he actually synthesized the polymer from simple chemical substances; he started from no polymer such as cellulose built up intricately by nature, but from such everyday, simple chemicals as phenol and formaldehyde.

EARLY RESEARCH IN POLYMERS

The polymers that were made, whether by modifying a natural polymer, or by entirely synthesizing the polymer, possessed valuable attributes, and the main of these was strength. Strength is a property that was signally absent from all of the organic chemists' ordinary preparations. Inorganic substances such as the metals and the stones furnished the strong materials, and most of our buildings were constructed of metal, stone, brick, and wood. Some of the organic materials that occurred in nature such as wood, silk, cotton, wool, and flax had great strength, but there was nothing that the organic chemist could synthesize in his laboratory which had any pretension to strength. Bakelite was the first exception; it was strong and it was a synthetic organic product. The waxes, the higher alcohols, acids, and esters all were devoid of real strength. What strength is there in a lump of naphthalene?

Polymers, largely because of their awkward habit of giving variable results, were frowned on, or at least avoided, by the majority of chemists, who thought that polymers had variable and unorganized structures. Variable, within limits, they were, but unorganized not at all. The organization displayed in the chemical structure of those natural polymers that we have since been able to elucidate far transcends in complexity and beauty the organization of the best of our man-made polymers.

Carothers' Work. The stuffy, unenlightened atmosphere which enveloped the chemistry of polymers persisted longer and later than it should have done; the subject fell, entirely through neglect, below the general level of advancement of science. When ultimately one very good chemist was able to see that polymers were the type of compound that constituted our everyday materials, and was bold enough to embark deliberately on research into their nature and synthesis, results came rapidly and the subject made enormous strides in a very short time. That the particular chemist was W. H. Carothers and that he had at his disposal the laboratories, the chemists, the engineers, and the materials with which his employers, E. I. du

Pont de Nemours & Co., supplied him, certainly hastened the work and enhanced its harvest in quality and in quantity. Even so, it is likely that if, at about the relevant time—the late twenties and very early thirties—any competent chemist had had the courage to tackle such a difficult subject, he would have achieved outstanding and remarkable results.

Work carried out a little earlier than that period by physicists, notably by O. L. Sponsler and his colleagues, gradually affirmed that cellulosic materials such as wood and the fiber ramie and cotton itself were built of molecules that were extremely long. They were natural polymers, but polymerization had taken place in one dimension only, so that molecules like long strings had come about.

Carothers, of course, knew of this, and he set out to make similar polymers in the laboratory. Polymers of the type we are considering—those having molecules which are like long strings and are not flat like a film nor solid like a brick—are known as "linear" polymers.

SYNTHESIS OF POLYESTERS

With the simplicity of genius Carothers saw straight to the heart of the problem. But it needed his painstaking and meticulous laboratory technique to resolve his theoretical views into practical results. He reasoned that just as a simple alcohol and a simple acid will react to form an ester, in the following way,

$$\underset{\text{Methyl alcohol}}{CH_3OH} + \underset{\text{Acetic acid}}{HOCOCH_3} \rightarrow \underset{\text{Methyl acetate (an ester)}}{CH_3OCOCH_3} + H_2O$$

so if he took a substance such as hexamethylene glycol, $HO(CH_2)_6OH$, which had a hydroxyl group at each end of its molecule and an acid such as adipic acid, $HOCO(CH_2)_4COOH$, which had an acid (carboxyl) group at either end of *its* molecule and combined them, then the reaction might go on indefinitely.

The following stages can be expected successively:

$$\underset{\text{Hexamethylene glycol}}{HO(CH_2)_6OH} + \underset{\text{Adipic acid}}{HOCO(CH_2)_4COOH} \rightarrow$$

$$HO(CH_2)_6OCO(CH_2)_4COOH + H_2O \quad (1)$$

Then two molecules of the product from (1) would react as follows:

$$HO(CH_2)_6OCO(CH_2)_4COOH + HO(CH_2)_6OCO(CH_2)_4COOH \rightarrow$$
$$HO(CH_2)_6OCO(CH_2)_4COO(CH_2)_6OCO(CH_2)_4COOH + H_2O \quad (2)$$

Two molecules of the product from (2) would react to form a molecule nearly twice as long. (3)

Two molecules from (3) would combine to form a molecule nearly twice as long again. (4)

The molecular weights of the starting materials are, respectively, 118 for the hexamethylene glycol and 146 for the adipic acid. Molecular weights rise in the above reactions as follows:

$$118 + 146 \rightarrow 246 + 18 \text{ (water)} \quad (1)$$
$$2 \times 246 \rightarrow 474 + 18 \text{ (water)} \quad (2)$$
$$2 \times 474 \rightarrow 930 + 18 \text{ (water)} \quad (3)$$
$$2 \times 930 \rightarrow 1842 + 18 \text{ (water)} \quad (4)$$

It is very clear that when the reaction has been carried on for a few stages further, molecules with molecular weights of 10,000, 20,000, 50,000, and 100,000 will be appearing. It is molecules of such size, with molecular weights between 10,000 and 200,000, that make up those natural polymers with which we are so familiar.

But although it is easy to write equations for such reactions, it was by no means easy to get them to go in the laboratory. Until a proper technique for their preparation (which is simple enough today) had been devised and established, there were many things that could go wrong. The polymers could oxidize and discolor and eventually char; sometimes polymerization proceeded in such a way that it formed molecules that were rings and not long chains; sometimes the polymerization stopped at a fairly early stage and could not be induced to go further.

Carothers in fact started to work on glycols and diacids to make polyesters, and he certainly made polyesters that had a much higher degree of polymerization than any polyesters previously made. They were not, however, entirely satisfactory and there was often a good deal of difficulty about the later stages of polymerization. Attention was then turned to using amide instead of ester formation as the basic reaction.

SYNTHESIS OF POLYAMIDES

Just as ammonia and acetic acid can be converted into acetamide,

$$NH_3 + \underset{\text{Acetic acid}}{HOCOCH_3} \rightarrow \underset{\text{Acetamide}}{NH_2COCH_3} + H_2O$$

so can an amine and acetic acid be converted into a substituted acetamide:

$$C_2H_5NH_2 + HOCOCH_3 \rightarrow \underset{\text{N-ethyl acetamide}}{C_2H_5NHCOCH_3} + H_2O$$

So, too, can an amino acid which combines the amino —NH_2 and the carboxyl —COOH groups on the same molecule, polymerize linearly, the carboxyl group on one molecule reacting with the amino group on another, thus:

$$\underset{\epsilon\text{-Aminocaproic acid}}{NH_2CH_2CH_2CH_2CH_2CH_2COOH} +$$
$$NH_2CH_2CH_2CH_2CH_2CH_2COOH \rightarrow$$
$$\underset{\text{Dimer}}{NH_2CH_2CH_2CH_2CH_2CH_2CONHCH_2CH_2CH_2CH_2CH_2COOH} + H_2O$$

The product, which consists of two molecules of aminocaproic acid which have condensed together with the elimination of water, is known as a *dimer*. Two molecules of the dimer can then condense to give one molecule of a *tetramer:*

$$\underset{\text{Dimer}}{NH_2(CH_2)_5CONH(CH_2)_5COOH} +$$
$$NH_2(CH_2)_5CONH(CH_2)_5COOH \rightarrow$$
$$\underset{\text{Tetramer}}{NH_2(CH_2)_5CONH(CH_2)_5CONH(CH_2)_5CONH(CH_2)_5COOH} + H_2O$$

And so the process goes on, the molecules condensing together to give longer and longer molecules, and when

about fifty or a hundred have condensed together, the linear polymer—then said to have a degree of polymerization of 50 or 100—develops good fiber-forming properties.

POLYMERIZATION OF HYDROCARBONS

The reaction whereby methyl chloride is converted into ethane by treatment with sodium,

$$\underset{\text{Methyl chloride}}{CH_3Cl} + 2Na + CH_3Cl \rightarrow \underset{\text{Ethane}}{CH_3CH_3} + 2NaCl$$

is well known; probably it is one of the first of the reactions taught the new student in organic chemistry. This same reaction can be modified to give high polymers. If, for example, there is a chain of $—CH_2—$ groups and at either end of the chain there is a halogen atom, then such a substance, on treatment with sodium, should yield a high polymeric hydrocarbon. Carothers appreciated this possibility and selected decamethylene dibromide as his starting material. This substance

$$BrCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2Br$$

has a suitably long chain of methylene groups and the bromine atoms at either end ensure that it will be reactive. In fact, by treating this substance in ethereal solution with metallic sodium, Carothers obtained long polymers, although the product was always a mixture of hydrocarbons ranging from decane, $CH_3(CH_2)_8CH_3$, to heptacontane $CH_3(CH_2)_{68}CH_3$. Some still higher members of the series $H—((CH_2)_{10})_n—H$ were apparently formed during the reaction but it was not possible to isolate them. Nevertheless the isolation of heptacontane, which has a molecular weight of 982, was a considerable achievement. Heptacontane is a waxy substance melting at about 105°C., soluble in butyl acetate, and distilling from a good vacuum at about 300°C. It is quite a high linear polymer, but not sufficiently high to show fiber-forming properties.

But although Carothers was unable to make fibers by this technique, *i. e.*, by using the reaction:

$$n\text{Br}(CH_2)_{10}\text{Br} + 2n\text{Na} \rightarrow \text{H}\,((CH_2)_{10})_n\text{H} + 2n\text{NaBr}$$

(The hydrogen atoms probably are provided by traces of moisture with which the system will be contaminated and which will react with traces of sodium to give the hydrogen occupying the terminal chain positions; alternatively the ether may take part in the reaction.)

yet the idea was right in principle. It has, for example, been shown since that when ethylene gas is subjected to very high pressures it will condense to polyethylene of very high molecular weight,

$$n\text{C}_2\text{H}_4 \rightarrow \text{H}(—CH_2CH_2CH_2CH_2 \ldots\ldots CH_2—)_{2n}\text{H}$$

and this polyethylene is a waxy solid, just as Carothers' heptacontane was, but it has a somewhat higher melting point and when melted draws out into fibers readily; indeed, several fibers spun from polyethylene have been on the market for some years. If the linear polymer is long enough, then it will form fibers. The properties of the fibers (solubility, melting point, chemical and biological resistance, strength, extensibility and so on) will depend on the nature of the groups which build up the chains, but their outstanding property, fibrosity itself, depends solely on the existence of linear polymeric molecules of sufficient length.

CONDENSATION POLYMERIZATION

Those ways of polymerizing that we have so far discussed are *condensation* polymerization, so called because the small molecules, the monomers, condense with each other with the liberation or splitting off of a molecule of water (or hydrochloric acid or similar simple compound). All of this type are known as condensation polymerizations. This is a main group of polymerizations and there are three main types of polymerization reaction that fall into this group; they are, first, *the simple type*, wherein one molecule carries on either end the two dissimilar reactive groups. ϵ-Aminocaproic acid, whose polymerization has just been discussed, is a typical example. Its full polymerization to a long polymer may be written

$$\underset{\text{Amino acid}}{n\text{COOH}(CH_2)_5\text{NH}_2} \rightarrow \underset{\text{Polyamide}}{\text{HO}(—\text{CO}(CH_2)_5\text{NH}—)_n\text{H}} + (n-1)\text{H}_2\text{O}$$

In an exactly similar way a hydroxy acid would condense to give a polyester, *e. g.*, ϵ-hydroxycaproic acid would condense in this way:

$$\underset{\text{Hydroxy acid}}{n\text{COOH}(CH_2)_5\text{OH}} \rightarrow \underset{\text{Polyester}}{\text{HO}(—\text{CO}(CH_2)_5\text{O}—)_n\text{H}} + (n-1)\text{H}_2\text{O}$$

Rather oddly, this, the simplest (on paper) of the three types of condensation polymerization, is not used at all on an industrial scale for the manufacture of any fiber-forming linear polymer. The reason doubtless is that α,ω-amino acids and hydroxy acids are relatively difficult and expensive to prepare and to isolate.

The second type of condensation reaction is that in which the different mutually reactive groups occur not on the same but on different molecules. Instead, for example, of condensing an amino acid we can condense a diamine and a diacid; the most familiar example will be that of hexamethylene diamine and adipic acid, which yields standard nylon according to the equation

$$\underset{\substack{\text{Hexamethylene}\\\text{diamine}}}{n\text{NH}_2(CH_2)_6\text{NH}_2} + \underset{\text{Adipic acid}}{n\text{COOH}(CH_2)_4\text{COOH}} \rightarrow$$

$$\underset{\text{Nylon}}{\text{H}(—\text{NH}(CH_2)_6\text{NHCO}(CH_2)_4\text{CO}—)_{2n}\text{OH}} + (2n-1)\,\text{H}_2\text{O}$$

Similarly, ethylene glycol and terephthalic acid condense to give the polyester which is known as Terylene in England and as Dacron in America (the two names are used for the same product).

$$\underset{\substack{\text{Ethylene}\\\text{glycol}}}{n\text{HO}(CH_2)_2\text{OH}} + \underset{\substack{\text{Terephthalic}\\\text{acid}}}{n\text{COOH}—C_6H_4—\text{COOH}} \rightarrow$$

$$\underset{\text{Dacron}}{\text{H}(—\text{O}(CH_2)_2\text{OCO}—C_6H_4—\text{CO}—)_{2n}\text{OH}} + (2n-1)\text{H}_2\text{O}$$

The industrial adoption of this method of condensation

polymerization for two main fibers is owing mainly to the greater ease and cheapness with which glycols (dihydric alcohols) and dicarboxylic acids can be prepared than can α,ω-amino acids or α,ω-hydroxy acids.

The third type of condensation polymerization is that whereby a reagent abstracts, and combines with, the end groups from the reacting and polymerizing molecules. The polymerization of decamethylene dibromide in the presence of sodium, already discussed, is a typical instance of this class. The sodium atoms combine with the bromine atoms on the halide and enable the residues to join up, thus:

$$Br(CH_2)_{10}:\underset{\cdot\cdot\cdot\cdot\cdot\cdot}{\overset{\cdot\cdot\cdot\cdot\cdot\cdot}{Br}} + \underset{\cdot\cdot\cdot\cdot\cdot\cdot}{\overset{\cdot\cdot\cdot\cdot\cdot\cdot}{Na}}: + :\underset{\cdot\cdot\cdot\cdot\cdot\cdot}{\overset{\cdot\cdot\cdot\cdot\cdot\cdot}{Na}} + \underset{\cdot\cdot\cdot\cdot\cdot\cdot}{\overset{\cdot\cdot\cdot\cdot\cdot\cdot}{Br}}:(CH_2)_{10}:\underset{\cdot\cdot\cdot\cdot\cdot\cdot}{\overset{\cdot\cdot\cdot\cdot\cdot\cdot}{Br}} + \underset{\cdot\cdot\cdot\cdot\cdot\cdot}{\overset{\cdot\cdot\cdot\cdot\cdot\cdot}{Na}}: +$$

$$:\underset{\cdot\cdot\cdot\cdot\cdot\cdot}{\overset{\cdot\cdot\cdot\cdot\cdot\cdot}{Na}} + \underset{\cdot\cdot\cdot\cdot\cdot\cdot}{\overset{\cdot\cdot\cdot\cdot\cdot\cdot}{Br}}:(CH_2)_{10}\,Br \rightarrow Br(CH_2)_{10}\,(CH_2)_{10}\,(CH_2)_{10}\,Br$$

or $Br\,(CH_2)_{30}Br$

ADDITION POLYMERIZATION

Although condensation polymerization reactions include the preparation of a large number of linear polymers, there is another large group known as addition polymerizations, by which linear polymers are made.

Typical of this type is the polymerization of ethylene to polyethylene, the transformation of the light, almost odorless, colorless gas to a hard, strong, waxy solid. Probably the first step here is the formation of 1-butene

$$CH_2{=}CH_2 + CH_2{=}CH_2 \rightarrow CH_2{=}CHCH_2CH_3$$

and the second step is the formation of 1-hexene:

$$CH_2{=}CHCH_2CH_3 + CH_2{=}CH_2 \rightarrow CH_2{=}CHCH_2CH_2CH_2CH$$

and so the process goes until ultimately it may be represented thus:

$$nCH_2{=}CH_2 \rightarrow CH_2{=}CH(CH_2)_{2n-3}CH_3$$

As G. S. Whitby and M. Katz have suggested, the polymerization of vinyl compounds (ethylene is typical of these) is "best represented as proceeding stepwise by the addition regularly of successive molecules of monomer to the double bond present at each stage of the polymerization immediately preceding."

The polymerization of vinyl compounds is extremely susceptible to catalytic action and as a rule oxygen and peroxides are catalysts, while antioxidants will inhibit polymerization. Light stimulates the process.

The mechanism outlined above of chain formation by a process of "one and one and one and one . . ." might delight the creator of the White Queen, but it is nevertheless a process of great speed and certitude and one, moreover, which is ideally disposed to result in the formation of linear polymers; there is no obvious opportunity, and little tendency in practice, for any departure from the linear form of polymerization.

Linear polymerization of vinyl compounds has proved to be a very rewarding process in the development of fibers. Acrylonitrile or vinyl cyanide has been one of the most useful of the vinyl compounds to polymerize. The polymer which has the constitution

$$NCCH{=}CH(CHCNCH_2)_nH$$

has been made and sold under the name of Orlon by E. I. du Pont de Nemours & Co.; it is a fiber that has outstanding chemical resistance so that it has been used for filter cloths, protective clothing, etc., and also has remarkable weathering qualities. Orlon will withstand exposure to tropical sunlight or the fumes of an industrial atmosphere and will even withstand burial for months in tropical soil, whereas a good heavy cotton fabric will disintegrate completely in a week when buried under similar conditions. Two other fibers, Acrilan and X-51, both of which have appeared fairly recently, are composed mainly of polyacrylonitrile, although in each, another, minor constituent has been co-polymerized with the acrylonitrile.

Polyvinyl chloride, formed simply by the polymerization of vinyl chloride according to the equation

$$\underset{\text{Vinyl chloride}}{nCH_2{=}CHCl} \rightarrow \underset{\text{Polyvinyl chloride}}{ClCH{=}CH(ClCHCH_2)_nH}$$

is the essential constituent of PCU fiber which is made by the Badische Anilin und Soda Fabrik, and of Rhovyl and some closely related fibers made in France.

Often better results from the standpoint of fiber properties are achieved if not just one but two or three substances are co-polymerized. For example, when vinyl chloride and vinyl acetate are co-polymerized, the product is superior in some respects to polyvinyl chloride, polyvinyl acetate, or a mixture of polyvinyl chloride and polyvinyl acetate. Thus polyvinyl chloride alone is a hard, tough resin which must be plasticized for extrusion purposes because it has a low decomposition temperature. Polyvinyl acetate is a clear resin of good acetone solubility but one which softens just above room temperature. Mixtures of polyvinyl chloride and polyvinyl acetate have never displayed any very promising properties, but co-polymers produced by the simultaneous polymerization of mixtures of monomeric vinyl chloride and monomeric vinyl acetate have quite different and very useful properties.

Thus a co-polymer of 88 per cent vinyl chloride and 12 per cent vinyl acetate is known as Vinyon and Vinyon HH and was one of the first of the truly synthetic polymers; its constitution is approximately

$$ClCH{:}CH\,(CHClCH_2CH(OCOCH_3)CH_2)_nH$$

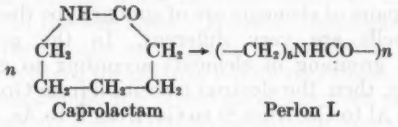
Another co-polymer, one of 60 per cent vinyl chloride and 40 per cent acrylonitrile is known as Dynel and Vinyon N. Dynel has proved to be very popular and blankets that seem to be well liked have been made from it.

Another co-polymer is Saran, this one a co-polymer of 85 parts vinylidene chloride, 13 parts vinyl chloride, and 2 parts acrylonitrile. It has been used for making Velon and Tygan fabrics; these can be washed and have been used for car upholstery and even for upholstering public service vehicles, although for this last purpose

they have the serious disadvantage of melting locally if touched with a lighted cigarette.

These additional polymerizations include many of great industrial value. They all depend on the rearrangement of the valence bonds in ethylenic or vinyl compounds.

The second class of addition polymerization reactions is one wherein a ring compound breaks and the individual units join together linearly. Caprolactam provides an example: it is a seven-atom ring compound which on being suitably heated forms a linear polymer and in so polymerizing behaves as if it were ε-aminocaproic acid, of which indeed it is the internal anhydride. The reaction that takes place is:



Caprolactam Perlon L

This particular process is actually used in Germany to make Perlon and in Japan to make Amilan. These fibers are similar to each other and are not unlike standard nylon except for their very much lower melting point, a serious disadvantage.

A third type of addition polymerization reaction is that wherein the end groups on the reacting monomers add on to each other to produce quite new groups. An example is the reaction of an isocyanate with an alcohol to form a urethane, thus:

$$\underset{\text{Isocyanate}}{RNCO} + \underset{\text{Alcohol}}{HOR'} \rightarrow \underset{\text{Urethane}}{RNHCOOR'}$$

When the reacting monomers are hexamethylene diisocyanate and tetramethylene glycol, their reaction gives rise to a linear polymer which is a polyurethane, manufactured in Germany under the name Perlon U.

Linear polymers were not understood until the twenties; they were not made until the thirties; but nowadays they are the foundation of a large and flourishing synthetic fiber industry, an industry which already produces some 300 million pounds of valuable fibers in a year, and one which will within a few years have doubled this already high production.

APPARATUS FOR DEMONSTRATING PAPER CHROMATOGRAPHY

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A SIMPLE and convenient arrangement for demonstrating paper chromatography comprises a jar, a solid rubber stopper to fit, and an alligator clamp of the type shown in the accompanying figure. A hole is drilled part way through the stopper from the midpoint of the bottom side, and the back end of the clamp is inserted in this hole. Strips of paper of suitable length may now be placed in the jaws of the clamp while the latter, along with the stopper, is readily held and opened with one hand.

This combination centers the strips with respect to the jar so that they do not stick to the sides, encloses the system tightly so that there is no evaporation from the paper strips, and assures reproducible results by standardizing the conditions. The figure shows 32-ounce, wide-mouthed bottles, 6¾ inches tall (a one-quart mayonnaise jar is good), size No. 11½ rubber stoppers, and No. 60 Series Weller alligator clips, but of course the actual dimensions are unimportant as long as there is sufficient distance from the clamp to the bottom of the jar to allow satisfactory development of the chromatogram.

In this particular setup, with about ¼ inch of water in the bottom of the jar, 5-inch strips of qualitative filter paper are of an appropriate length, and such substances as inks, dye mixtures, and inorganic ions are

readily chromatographed in 10–20 minutes. A set of four bottles is convenient for comparison of a number of different substances.

ELECTRONEGATIVITIES IN INORGANIC CHEMISTRY. III

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THE preceding papers (*1*, *2*) of this series have described some ideas concerning the nature of chemical combination from which it has been possible to evaluate the electronegativities of atoms alone or combined, of molecules, and of simple and complex ions. From these values the charges on the individual atoms in any combination can be estimated.[1] Information on the electronegativities and charge distribution, even though somewhat speculative, can be extremely useful. The purpose of this paper is to illustrate some of the practical applications of such information to interpreting the facts of inorganic chemistry.

CHEMICAL VARIATIONS IN THE PERIODIC TABLE

Electronegativities and Electronic Configurations. Ideally, it would be very useful to be able to group the elements according to electronic configurations and also physical and chemical properties, in such a manner that uniform transitions or relationships were shown. Unfortunately, however, transitions in properties are not as uniform as could be wished, and the periodic table gives an impression of system and orderliness which is somewhat illusory.

Consider, for example, the so-called major groups of elements. Electronically, the only groups of closely similar elements are the inert elements, the alkali metals, and the alkaline earth elements including beryllium and magnesium. The inert elements have in common very stable outermost shells with 8 electrons, except for helium. The alkali metals have in common the inert element structure plus one electron in the next principal quantum shell. The alkaline earth metals have in common the inert element structure plus two electrons in the next principal quantum shell. Even in these, the chemistry of the first member of each group, whose ion has an outermost shell of two instead of eight, is notably different from that of the following members. All the other "major groups" have more profound changes in electronic configuration, however, and are more arbitrarily selected. In Group III, for example, the change from aluminum to scandium is not the same as from sodium to potassium or magnesium to calcium, because the valence electrons of scandium differ from those of aluminum, even though the underlying structures are both of inert element type. On the other hand, the grouping of gallium with aluminum is no more logical, from an electronic viewpoint, than the grouping of copper with sodium or zinc with magnesium. Although the valence electrons of these pairs of elements are of similar type the underlying shells are very different. In the generally accepted grouping of elements according to greatest similarity, then, the electron transition from Group III on, from Al to Ga, from Si to Ge, from P to As, from S to Se, and from Cl to Br, is from an 8-shell to an 18-shell type of atom.

It is customarily considered that the properties of the elements in a major group change, not necessarily uniformly, but fairly consistently, with increasing atomic number, weight, and size, and that a fundamental change is toward decreasing electronegativity. As has been recently pointed out, however, the electronegativity as measured by stability ratios actually alternates with increasing atomic number within a major group, and in particular, the transition from an 8-shell to an 18-shell type of atom results in an *increase* in electronegativity. In the filling of the outer shell from copper to bromine, the 18-shell atoms become increasingly like 8-shell atoms. Therefore this increase in electronegativity is greatest between sodium and copper and diminishes from left to right across the periodic table, disappearing in the halogens.

Explanations of Chemical "Anomalies." It has recently been demonstrated (*3*) that many chemical facts which have always appeared anomalous in the light of previously accepted ideas of decreasing electronegativity within a major group may be explained at least partially by the help of the new electronegativity values and concepts. Reference is made to the original paper on this subject for details, some of which will be mentioned briefly here, with a few additional data.

The alternating trends of electronegativity of the elements are depicted in Figure 1. When these trends are recognized, it becomes easier to understand why, for example, the oxide of aluminum has a much higher heat of formation than the oxides of either boron or gallium, or why the chemistry of germanium resembles that of carbon more closely than the chemistry of silicon does, or why arsenic, in contrast to both phosphorus and antimony, forms no pentachloride. In the latter compounds, for example, the partial charge on chlorine would be -0.08 in both PCl_5 and $SbCl_5$, neither of which is very stable, but only -0.05 in $AsCl_5$—not a

[1] All charges in this paper are based on assumed 90 per cent polarity of NaF. In some respects, 75 per cent may be preferable. This would have no effect on interpretations or conclusions, but would alter all numerical charge values by a factor of 0.83. *SR* values of anions would be a little lower and of cations a little higher.

large difference but significant of the even lower stability expected of $AsCl_5$. The low degree of satisfaction gained by the chlorine in PCl_5 and $SbCl_5$, moreover, is in accord with their properties of thermal instability and activity as chlorinating agents.

It is interesting to note the alternations in the properties of the trichlorides of the Group V-A elements, as given in Table 1. These are of the type observed by Hildebrand (*4*) many years ago, and are readily compatible with the electronegativity and partial charge values.

NONPOLAR BONDS

There are really very few bonds which are entirely nonpolar, except those between atoms of the same element in the free state. However, electronegativity values permit the recognition of a number of compounds in which the polarity is only very slight. About such compounds, the observation has been made (*5*) that their thermal stability appears to diminish with increasing radius difference between the combined atoms.

For example, the covalent hydrides of least polarity in order of increasing radius difference, are CH_4, PH_3, GeH_4, HI, H_2Te, SbH_3, BiH_3, PbH_4, and HgH_2. Data are not available for a complete comparison, but this list appears to represent also the approximate order of decreasing thermal stability. Methane is stable to about 800°C., and germane only to about 285°, at which temperature hydrogen iodide is about 17 per cent dissociated. Hydrogen telluride decomposes slowly at ordinary temperatures. Stibine is much less stable than phosphine, and bismuthine still less. Plumbane decomposes at 0° and mercuric hydride evidently does not exist above −80°.

Another interesting example is the iodides of sulfur, selenium, and tellurium, which would be expected all to be nearly nonpolar. The iodine atom (atomic radius 1.33 Å.) resembles the tellurium atom in size but is considerably larger than the selenium atom (1.16 Å.) and the sulfur atom (1.02 Å.) Tellurium iodide appears to be the only compound of this group stable enough to be isolated, and sulfur iodides are unknown.

Except the fluoride, the nitrogen halides are notoriously unstable, but the least stable appears to be the bromide. This irregularity may be correlated with the fact that the bonds are nonpolar in the bromide but strengthened by some polarity in both chloride and iodide. The partial charge on nitrogen is only about 0.01 in the bromide but −0.13 in the iodide and 0.09 in the chloride. The radius of bromine, 1.14 Å., is much larger than that of nitrogen, 0.75 Å. The same general principle appears applicable to the relative instability of carbon tetraiodide and the nonexistence of carbon di elluride, both iodine and tellurium being similar to carbon in electronegativity but having much larger atoms.

It should be noted that even between atoms identical in radius, nonpolar covalent bonds are weaker with increasing radius, corresponding to increasing principal quantum number of the valence shell. Thus the heat of atomization of gaseous Li_2 is 26.54 kg.-cal./mol and only 10.66 kg.-cal./mol for Cs_2: values for Cl_2 and I_2 are 58.02 and 36.09. There is also some indication that highly polar bonds may be weaker between atoms differing widely in radius. Thus CsH, in which the bond is 69 per cent ionic according to these methods, is less stable than LiH, in which the bond is 59 per cent ionic.

TABLE 1
Alternations in Group V-A Trichlorides

Compound	*SR*	*δCl*	*Hf° (g.), kg.-cal./mol*	*Av. bond energy, kg.-cal./mol*
NCl_3	4.82	−0.03	...	...
PCl_3	4.48	−0.12	−73.22	−78.48
$AsCl_3$	4.66	−0.07	−71.5	−73.06
$SbCl_3$	4.49	−0.11	−75.22	−74.34
$BiCl_3$	4.61	−0.08	−64.7	−67.14

ADJACENT POSITIVE CHARGES

The concept of equalized electronegativity within a molecule permits the recognition of covalent bonds between atoms which both bear positive charges. In general it seems reasonable to expect that the higher the partial positive charge on an atom, the less available its remaining electrons would be for bond formation.

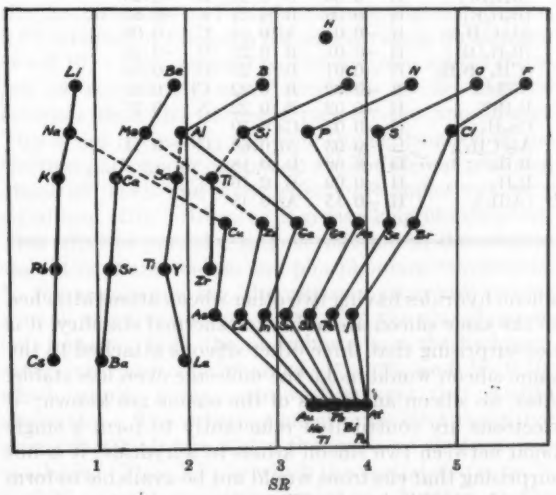

Figure 1. Electronegativities of Elements

In particular, it is observed that there are many compounds in which the existence of adjacent positive charges appears to be related to weakness of the bond and corresponding thermal instability. There are also nonexistent compounds which may be considered too unstable to be formed because they would involve bonds between atoms of appreciable partial positive charge. There are also a few notable exceptions, in which other factors appear to compensate for the expected weakening of a bond between two positively charged atoms.

Silanes and Silicones. Compounds of silicon with hydrogen differ greatly from compounds of carbon with hydrogen in that silicon-hydrogen bonds are much more polar, and in the reverse direction, than carbon-hydrogen bonds. In a molecule of formula $(CH_2)_n$, the partial charges would be −0.05 on carbon and 0.025 on hydrogen. In a molecule of formula $(SiH_2)_n$, the partial charges would be Si, 0.20, and H, −0.10. These values are consistent with the observed facts that carbon-carbon chains of indefinite length are possible in hydrocarbons but evidently not in hydrosilicons, which are not known beyond Si_6. Furthermore, branched-chain silicon hydrides are not known; if silicon hydrides having two other silicon atoms attached to the same silicon are of limited thermal stability, it is not surprising that three other silicons attached to the same silicon would make the molecule even less stable. Also, no silicon analogues of the olefins are known; if electrons are contributed reluctantly to form a single bond between two silicon atoms in a hydride, it is not surprising that electrons would not be available to form a stable double bond. There is no reason to expect that silicon-silicon bonds are inherently unstable; the instability in the hydrides seems to result from the relatively high partial positive charges on the silicon atoms produced by the hydrogen atoms.

TABLE 2
Partial Charges on Combined Atoms in Hydrogen Compounds

CH_3BF_2	H	0.13	B	0.39	C	0.05	F	−0.42
$[BHCl_2]$	H	0.12	B	0.38	Cl	−0.25		....
$C_2H_4O_2BH$	H	0.08	B	0.33	C	0.00	O	−0.35
$[BH_2F]$	H	0.07	B	0.32	F	−0.47		....
$(CH_3O)_2BH$	H	0.06	B	0.31	C	−0.01	O	−0.37
$(C_2H_5O)_2BH$	H	0.05	B	0.30	C	−0.03	O	−0.38
$(CH_3)_2BF$	H	0.04	B	0.29	C	−0.03	F	−0.49
$[BH_2OH]$	H	0.03	B	0.28	O	−0.39		
$[BH_2Cl]$	H	0.03	B	0.28	Cl	−0.33		
$C_6H_5BH_2$	H	0.01	B	0.26	C	−0.06		
$Ga(CH_3)_3$	H	0.01	Ga	0.12	C	−0.06		
$B(CH_3)_3$	H	0.00	B	0.24	C	−0.08		
$Al(C_3H_7)_3$	H	0.00	Al	0.65	C	−0.07		
$[BH_2Br]$	H	0.00	B	0.24	Br	−0.26		
$[B_2H_5F]$	H	0.00	B	0.24	F	−0.53		
$Al_2(C_2H_5)_6$	H	−0.01	Al	0.64	C	−0.08		
$[B_2H_5OH]$	H	−0.01	B	0.23	O	−0.43		
$(CH_3)_4B_2H_2$	H	−0.01	B	0.23	C	−0.08		
B_2H_5Cl	H	−0.02	B	0.22	Cl	−0.37		
B_3H_7N	H	−0.02	B	0.22	N	−0.27		
Ga_2H_6	H	−0.03	Ga	0.10		...		
$Al_2(CH_3)_6$	H	−0.03	Al	0.60	C	−0.11		
B_2H_6	H	−0.06	B	0.18		...		
B_5H_9	H	−0.09	B	0.16		...		
$(AlH_3)_x$	H	−0.15	Al	0.45		...		

A similar situation prevails in the completely methylated derivatives, where also the adjacent silicon atoms possess positive charge and long chains are thermally unstable (*6*). It is of interest to compare the very stable silicones. Here the alternating Si and O atoms are connected by bonds which are definitely polar, but here there are no adjacent atoms of positive charge. The *SR* of a methyl silicone polymer is 3.62. The Si-O chain is thus one of alternating polarity and the Si-C bonds are nonpolar bonds between carbon of −0.05 charge and silicon of 0.34 charge.

Oxyhalides. The nonexistence of compounds which might by ordinary standards be expected to be fairly stable can frequently be explained on the basis of adjacent positive charges. The thionyl and sulfuryl halides illustrate this. Thus in $SOCl_2$ the charges on S and Cl are 0.19 and −0.04. In $SOBr_2$, which decomposes below its boiling point, both S and Br are positive, the charges being 0.13 and 0.01. In SOI_2, which is unknown, the charges on S and I would be 0.03 and 0.11. Similarly, in SO_2Cl_2, the charges on S and Cl are 0.21 and −0.02, but in SO_2Br_2, which is unknown, the charges on S and Br would be 0.17 and 0.05. In the hypothetical SO_2I_2, the charge on S would be 0.08 and on I, 0.16. Another example is POI_3, where the charge on P would be 0.20 and on I would be 0.04. This compound is not known.

Disproportionation. Similar explanations apply to numerous compounds which although moderately stable, tend to disproportionate readily. For example, H_3PO_3 readily forms PH_3 and H_3PO_4. As indicated by the fact that H_3PO_3 is only a dibasic acid, one hydrogen atom is believed to be attached directly to the phosphorus. The charges on these atoms are, for H, 0.18, and for P, 0.25, which would contribute to the instability and promote the disproportionation to molecules not having adjacent, positively charged atoms.

Mixed halides, notably those of phosphorus, tend to disproportionate to give the simple halides. This reaction may well be promoted by the presence of adjacent positive charged atoms in the mixed halides. For example, in PF_3Cl_2 the charges on P and Cl are 0.51 and 0.02. This compound accordingly not only disproportionates to form PCl_5 and PF_5, but also reacts with metals as a chlorinating agent rather than a fluorinating agent. The chlorine atoms are less stable than in the elementary state, whereas the fluorine atoms are reduced already to a charge of −0.18, so that their bonds with the phosphorus are less readily broken.

Exceptions. When atoms having partial charge can approach closely within the same molecule even though there is no direct bond between them, electrostatic forces can be exerted between them. Under some circumstances this may compensate, at least partly, for the instability resulting from adjacent positive charges. The stable fluorocarbons appear to be an outstanding example (*7*). In a molecule of the formula $(CF_2)_n$, the partial charges on C and F are 0.36 and −0.18. Here the electrostatic attraction between carbon, and fluorine on adjacent carbon, appears more than adequate to compensate for the loss in stability associated with the adjacent positive charges on carbon atoms. This effect may be greatest when, as in the fluorocarbons, the oppositely charged atoms are very nearly of the same size.

Similarly, in any part of a molecule such as

if A and B are both positive and C is negative, and if A and C can come close together, the electrostatic attraction between A and C would be expected to help stabilize the molecule, counteracting the effect of a weakened bond between A and B.

ELECTRON-DEFICIENT COMPOUNDS AND DERIVATIVES

One of the most interesting applications of these ideas of electronegativity and charge distribution is to the intriguing problem of "electron-deficient" bonding, as illustrated by diborane, B_2H_6. It is now fairly generally accepted that two BH_3 groups are held together by a "hydrogen bridge," but the exact nature of this bridge has not been established. A study (*8*, *9*) of the charges on the atoms of such compounds has disclosed that wherever such a bridge is believed to occur, the partial charge on hydrogen is negative. When the charge on hydrogen is zero or positive, dimerization does not seem to occur. These observations include not only compounds such as diborane but also alkyl compounds such as boron and aluminum trimethyls, in which the bridging, when it occurs, may be similar.

Charge distribution data for a number of real and hypothetical compounds are given in Table 2. From these data and their implication as to the nature of the hydrogen bridge, it becomes understandable that $B(CH_3)_3$ and $Ga(CH_3)_3$, for example, are monomeric and resist hydrolysis, while $Al_2(CH_3)_6$ is a dimer and hydrolyzes extremely easily. The reason for the failure of $BH(OCH_3)_2$ to dimerize despite the presence of the necessary hydrogen atom and vacant orbital also seems clear. Further, numerous predictions are possible. For example, fluorodiborane is as yet unknown. The data of Table 2 suggest that it would be quite unstable if it could exist at all. Even the BFH_2 group, in which both H and B are appreciably positive, would be expected to disproportionate readily to form BF_3 and B_2H_6.

Too little is known about both hydrogen bonding and hydrogen bridge bonding to judge the significance of a direct comparison, but the similarity is interesting. A hydrogen bond appears to be a bond formed between a combined hydrogen atom bearing a partial positive charge and an atom with a partial negative charge which has available an orbital containing two unshared electrons. A hydrogen bridge bond appears to be a bond formed between a combined hydrogen atom bearing a partial negative charge and an atom with a partial positive charge which has available an orbital containing no electrons.

ACIDS, BASES AND RELATED PROBLEMS

The general subject of acids and bases and of electron donor-acceptor interaction is so broad in scope and so complex that it is difficult to establish clear-cut subdivisions even for purposes of discussion. Certain useful generalizations may be drawn, however, from a study of electronegativities and charge distribution within molecules. These are:

(1) The higher the electronegativity of a molecule, the greater the tendency to act as oxidizing agent or acid, and the less the tendency to act as electron donor.

(2) The lower the electronegativity of a molecule, the greater the tendency to act as reducing agent or base, and the less the tendency to act as electron acceptor.

(3) The greater the partial positive charge on an atom, the less available are its valence electrons either for ordinary covalent bond formation or for coordinate bond formation.

(4) The greater the partial negative charge on an atom, the more available are its valence electrons for bond formation, and, especially, the more readily the atom can act as electron donor.

(5) The complete equalization of electronegativities through a coordinate bond does not appear to be possible when the donor molecule is initially more electronegative than the acceptor.

Some applications of these generalizations are now discussed.

Nitrogen and Phosphorus as Electron Donors. From the fact that phosphorus is less electronegative than nitrogen, it might be expected to be a better electron donor. For example, the electronegativity of phosphine is 3.50 compared to 3.76 for ammonia. However the partial charge on P in phosphine is slightly positive, 0.05, whereas in ammonia the partial charge on nitrogen is −0.19. The unshared pair of electrons on the nitrogen is accordingly more available to an electron acceptor than the unshared pair on the phosphorus. This is not necessarily the complete explanation as the electron pairs under discussion are in different principal quantum levels and steric effects are sometimes very significant (*10*). However, it gives a helpful viewpoint. This effect of partial charge is reflected in the relative stabilities of ammonium and phosphonium compounds. In the ammonium ion, the nitrogen atom still retains a small negative charge, −0.03. In the phosphonium ion, however, both the phosphorus and the hydrogen atoms are positively charged, P, 0.25, and H, 0.19, which results in a much weaker bond that readily dissociates. The substitution of more electronegative atoms than hydrogen makes the unshared electrons less available. Thus NF_3, in which the partial charge on N is 0.25, is not an electron donor. Neither is the perfluoro derivative of trimethylamine, $N(CF_3)_3$, in which the charge on N is 0.17.

Oxides and Halides. The relative strengths of acids and bases are the result of a complex interaction of factors among which are electronegativities, hydration energies, steric relationships, and internuclear distances. It is of interest, therefore, that a rough relationship between electronegativities of oxides and their acidic, amphoteric, or basic properties can be demonstrated as in Table 3. Water itself is fairly high in electronegativity (4.04), but it can act as electron

TABLE 3
Electronegativities (*SR*'s) of Some Oxides

Na_2O 1.37	H_2O 4.04	As_4O_6 4.64
CaO 2.52	B_2O_3 4.08	CO_2 4.68
MgO 2.85	SiO_2 4.14	As_4O_{10} 4.80
Ag_2O 3.02	Ga_2O_3 4.30	SO_2 4.82
BeO 3.12	P_4O_6 4.36	SeO_2 4.86
Al_2O_3 3.47	SnO_2 4.38	SO_3 4.91
CdO 3.67	P_4O_{10} 4.59	SeO_3 4.95
ZnO 3.84	GeO_2 4.60	N_2O_5 4.99
TiO_2 3.95	TeO_2 4.61	Cl_2O_7 5.15
SnO 4.02		

donor since the unshared electrons of the oxygen are more available due to the relatively high partial negative charge of −0.30. It will be observed that oxides are predominantly or exclusively basic if their electronegativities are below about 3. At this value, acidic properties begin to show, and up to the value for water, the oxides become increasingly amphoteric. Oxides having values greater than that of water are predominantly acidic, and increasingly so with increasing electronegativity. Oxides of the larger atoms, however, may also show some basic properties even when the electronegativities are high. This may be explained as a result of a greater ease of separation into ions where the internuclear distance is greater, even when the polar character of the bond may be less.

The change from basicity toward acidity with increasing positive oxidation state may be illustrated by oxides of manganese. Using the uncertain value of 3.15 for the *SR* of Mn, the values for amphoteric MnO, almost wholly acidic MnO_2, and strongly acidic Mn_2O_7 are 4.05, 4.40, and 4.65. The corresponding partial charge on oxygen in the isolated molecules is −0.29, −0.20, and −0.16.

The combination of an acidic oxide with a basic oxide to form a salt may be described as the oxidation of the latter by the former, the acidic oxide having initially a higher electronegativity. The stability of the salt so formed will depend on the electronegativity difference between the oxides, and also, of course, on the state of oxidation or reduction of the individual elements.

The combination of simple binary halides to form complex halides is closely analogous to the combination of oxides. A binary halide of relatively high electronegativity may be expected to combine with a binary halide of relatively low electronegativity if coordination factors are favorable. For example, even though the octets about Sn and Cl in the stannic chloride molecule are presumably complete and the effective atomic numbers of inert elements are achieved, the molecule retains relatively high electronegativity, 4.50, with a charge of 0.46 on Sn. Since orbitals are available about the Sn atom, two chloride ions, of electronegativity 1.08, are readily coordinated to form the stable hexachlorostannate ion, $SnCl_6^{--}$. Here the electronegativity has been reduced to 3.60 and the partial charge on Sn to 0.17.

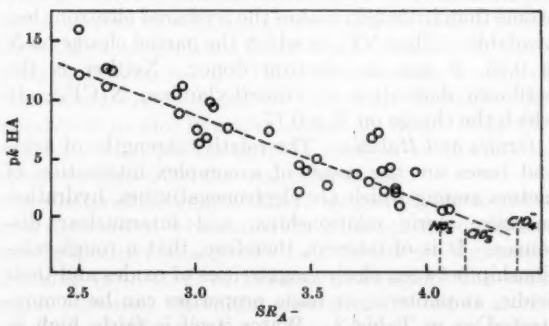

Figure 2. Relation of Acid Strength to Electronegativity of Acid Anion

Acid Strength. Hydrogen acids may be considered to be coordination compounds. The nucleus in these compounds is the hydrogen ion, which has a coordination number, in terms of coordination bonds, of one. An acid is then merely a coordination complex composed of one anion attached to one hydrogen ion. If the complex is relatively unstable in water solution, the acid is strong, and vice versa. Since the electron acceptor is the same for all these acids, the acid strength must depend on the donor. To the extent that other factors can be equalized or neglected, the more electronegative the anion the stronger the acid, because the more electronegative the anion, the less readily will it act as electron donor, forming a coordinate bond with the proton. There is no way in which other factors can be eliminated and as yet no way of taking them into account quantitatively. However, they can be considered partly equalized in a series of acids in each of which the acid proton becomes attached to oxygen. The relationship of electronegativity of the anion to acid strength for such a series is shown in Figure 2. It will be noted that although far from perfect, the trend of increasing acid strength with increasing anion electronegativity is unmistakable. It is especially interesting to note that all the oxygen acids which have very low or negative p*k* values, and none of the other oxygen acids, have anion electronegativities greater than the water molecule. In other words, perchloric, chloric, nitric, and sulfuric acids are very strong acids in aqueous solution apparently because their anions are poorer electron donors than water molecules—*e.g.*, hydronium ion is a stronger complex than $HClO_4$. In agreement with this observation is the fact that perchlorate and nitrate ions show little or no tendency to form complexes with any cations. The essential validity of the electronegativity values for the oxygen-containing anions appears to be supported by these data.

A series of acids which, although organic, illustrate the trend with a minimum of complicating factors, is composed of acetic acid and its halogenated derivatives. These are listed in Table 4.

In the nonoxygen acids, such as the hydrogen compounds of elements of Groups VI-A and VII-A, the atoms to which hydrogen becomes attached are all different, and other factors, such as internuclear distances and principal quantum level of electrons, become much more important. The anions of all these

TABLE 4
Effect of Anion Electronegativity on Acid Strength

Acid	*SR, Anion*	*Charge on O, Anion*	*pk*
CH_3COOH	3.53	−0.42	4.745
$CH_2ClCOOH$	3.72	−0.38	2.818
$CHCl_2COOH$	3.91	−0.33	1.292
CCl_3COOH	4.13	−0.27	0
CF_3COOH	4.42	−0.20	Neg.

acids are fairly low in electronegativity, yet the complex with the proton seems quite weak, especially in HI, HBr, and HCl.

Relative Stabilities of Acids and Their Salts. It is well known that in general, salts are much more stable than the free acids. The relative stabilities of free oxygenated acids and their salts are readily explained in terms of electronegativity. A free acid is a combination of hydrogen oxide (water) with a more electronegative oxide. Its salt is usually the combination of the same more electronegative oxide with an oxide less electronegative than water, giving much stronger interaction. If the latter oxide is not much less electronegative than water, the resultant salt may be relatively unstable.

Similarly, other complex acids are much less stable than their salts. For example, HCl of *SR* 4.19 is more electronegative than $AlCl_3$ of *SR* 3.91. Since any coordination of the two molecules must involve the Al atom as acceptor and a chlorine atom as donor, no stable complex acid, $HAlCl_4$, is expected. A chloride ion, however, with its unit negative charge and its *SR* of 1.08, is a much more effective electron donor than the chlorine atom of HCl. Accordingly, $AlCl_3$ readily coordinates with Cl^- to form the stable complex ion, $AlCl_4^-$. $AlCl_3$ therefore forms stable salts with chlorides of the more active metals. Likewise, neither fluoboric acid, HBF_4, nor fluosilicic acid, H_2SiF_6, are formed directly from HF and BF_3 or SiF_4. HF, with *SR* 4.52, would have only slight tendency to act as electron donor to BF_3 (4.82) or SiF_4 (4.92). However, fluoride ion, with *SR* 1.59 and unit negative charge, is a much better electron donor than HF, and very stable complex salts containing BF_4^- and SiF_6^{--} can be formed.

Addition Compounds. Of the same general Lewis acid-base type of reaction as those discussed above are the reactions of electron acceptors like BF_3 with electron donors like NH_3 to form addition compounds like $BF_3{:}NH_3$. It has been demonstrated by Brown and his co-workers (*10*) that the stability of such coordination bonds is often strongly influenced by steric factors, which help explain many otherwise anomalous facts. Aside from such factors, the general principles listed at the beginning of this section apply. Thus BF_3, of *SR* 4.82 and partial charge on B of 0.67, is a stronger acceptor than BCl_3, of *SR* 4.29 and charge on B of 0.49.

It has been reported (*11*) that the compounds with $N(CH_3)_3$ formed by BF_3, BF_2CH_3, $BF(CH_3)_2$, and $B(CH_3)_3$ have a coordination bond which is much weaker with substitution of the first methyl group for fluorine, and continues by smaller decrements to become weaker with each successive methyl substitution. Although steric factors may also be involved, this observation is entirely consistent with the electronegativity values of these molecules and the charge on the acceptor atom, as shown in Table 5.

TABLE 5
Electronegativity Difference and Stability of Addition Compounds

(Coordination with $N(CH_3)_3$, *SR* 3.66)

Compound	*SR*	*SR* − 3.66	*Charge on B*	*Stability increasing*
$B(CH_3)_3$	3.54	−0.12	0.24	↓
$BF(CH_3)_2$	3.69	0.03	0.29	
BF_2CH_3	3.98	0.32	0.39	
BF_3	4.82	1.16	0.67	

Coordination of a water molecule or hydroxide ion to a central atom of a molecule is often considered an essential preliminary to hydrolysis. This would explain, for example, the failure of such "coordinatively saturated" molecules as CCl_4 and SF_6 to hydrolyze. The rate of hydrolysis of otherwise similar molecules might therefore be expected to be related to the ability of these molecules to add water. Burg (*12*) has noted that the order of decreasing hydrolysis rate is POF_3, PSF_3, PSF_2Br, and $PSFBr_2$. He suggests increasing steric hindrance to base coordination as a cause. An alternative explanation is apparent from the electronegativities and charge on P in these molecules: 5.06, 0.53; 4.83, 0.46; 4.60, 0.39; and 4.38, 0.32.

Complex Ions. Closely related are the problems of complex ions, which are considered to be donor-acceptor combinations. A study of the assigned electronegativity values appears helpful in such problems. For example, why do cuprous and argentous ions form stable complexes containing only two (or less commonly, three) molecules of ammonia, when four molecules would provide not only a shared outer octet but also the effective atomic number of the next higher inert element? A comparison of the electronegativities of the different possible complexes suggests a possible partial explanation. Argentous ion, Ag^+, for example, has an *SR* of 4.94 compared to NH_3 with an *SR* of 3.76. It is reasonable that a molecule of ammonia would tend to act as electron donor in forming a coordinate bond with the argentous ion. The product, $Ag(NH_3)^+$, has an *SR* of 4.05, an appreciable reduction from 4.94, but still substantially higher than the value for ammonia. The charge on the silver atom has correspondingly been reduced from 1.00 to 0.66. The complex with one ammonia can form a coordinate bond with a second molecule of ammonia, the resultant ion, $Ag(NH_3)_2^+$, having an *SR* of 3.93, which is an appreciable reduction from 4.05. The charge on the silver atom has been reduced to 0.62. However, the addition of a third

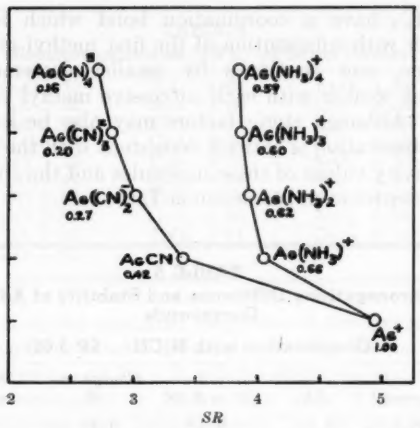

Figure 3. Electronegativities of Complex Ions, and Charge on Silver

ammonia molecule would only reduce the *SR* to 3.87, and a fourth to 3.85. The charge on silver would only be reduced to 0.60 and 0.59. This suggests that Ag^+ takes on two ammonia molecules most stably because further addition of ammonia would contribute only negligibly to its stabilization.

In a similar manner, it can be shown that by coordination with cyanide ion, Ag^+ is reduced in *SR* to 3.40 by the first, 3.02 by the second, 2.83 by the third, and 2.72 by the fourth. One might reasonably expect from these data that stable complexes of argentous and cuprous ions with two, three, and four cyanide ions could exist. Actually, the most stable complexes are of two and three cyanide ions per argentous ion, but with cuprous ion the four-cyanide complex is also stable. As might be expected, the higher electronegativity of the Ag^{++} ion causes its coordination number to be characteristically four. Similarly, the formation of $Cd(NH_3)_4^{++}$ and $Co(NH_3)_6^{+3}$ may be explained. The relationship among coordination number, actual charge on central atom, and electronegativity of complex is shown in Figures 3 and 4. No claim is intended that these are complete explanations.

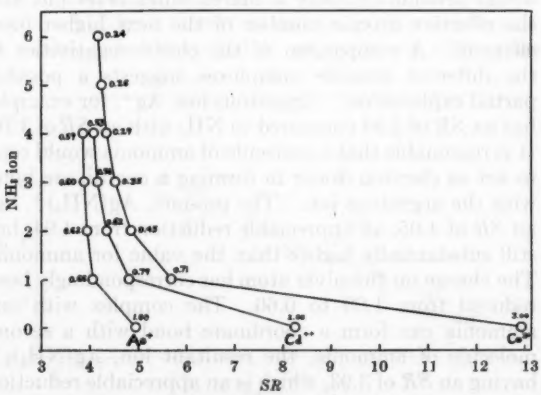

Figure 4. Charges on Central Atom, and Electronegativities of Some Complex Ammines

In some complexes, other factors doubtless may be of equal or greater importance. These ideas merely provide one more possible aid to understanding.

Stabilization of Oxidation States. The concept of equalized electronegativity in molecules or complex ions may help to explain the nature of oxidation states and their stabilization through complex formation. The usefulness of oxidation numbers is well established. Sometimes, however, there is a tendency to lose sight of the artificiality of the concept of oxidation state, to fail to recognize that the same formal oxidation state may mean entirely different actual conditions of oxidation in two different molecules. This is well illustrated by the charges on phosphorus (V) in PCl_5 and on phosphorus (III) in PF_3, which are 0.40 and 0.52. The P (III) is actually more oxidized than the P (V). According to these ideas, the so-called "stabilization of oxidation states" is usually actually a change in the condition of the atom with respect to oxidation, to a condition of lesser chemical activity, without changing the conventionally assigned oxidation number. Thus, for example, the cobaltic ion, Co^{+3}, with its effective electronegativity of about 13 undoubtedly reduced by hydration, still readily oxidizes water, liberating oxygen. When it has become coordinated with six molecules of ammonia, however, the oxidation state of plus 3 is still assigned to it although its actual state is indicated by the electronegativity of the complex ion, which is only 4.16, and by the calculated partial charge on the cobalt atom, which is only 0.24 instead of 3.00. On the other hand, the cobaltous ion, Co^{++}, is stable toward oxidation when not stably complexed, but in combination with ammonia as $Co(NH_3)_6^{++}$, with electronegativity reduced to 4.02 and charge on Co only 0.20, it is easily oxidized by air to the $Co(NH_3)_6^{+3}$ ion. In its complex with cyanide ion, $Co(CN)_6^{-4}$, the electronegativity of the cobalt is so low, 2.99, that it is easily oxidized even by water (4.04) to the "plus 3 oxidation state" where its electronegativity is still only 3.24. The strong reducing property of the cobaltous cyanide complex is to be expected from the charge calculated for the cobalt atom, which is -0.13 and changes to 0.05 in the Co (III) complex.

SUMMARY

The object of this work has been to recognize some simple correlating principles leading to improvement in the organization and unification of the science of inorganic chemistry. A method has been developed for determining the relative electronegativities of atoms, molecules, and ions, and for estimating the partial charge on combined atoms. Methods of applying this information toward an understanding of ordinary chemical phenomena have been suggested.

No one who studies these problems can fail to appreciate the wisdom and accuracy of the statement, "It is we who are simple, not nature." This very fact, however, requires a compromise between absolute accuracy and practical understanding. A complete explanation of even the least complex of chemical phenomena would

probably be complicated beyond man's comprehension. An explanation which is simple and readily understandable is almost certain to be oversimplified. This, however, does not prevent its being useful if it is not inconsistent with ordinary logic and elementary fact, or with basic accepted theory. It is believed that the ideas presented in these three papers may be very useful in the teaching of inorganic chemistry, especially at an advanced level. If in some respects they are inadequate, it is hoped that their presentation here will stimulate further developments in this field.

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A THERMOSTATIC AIR BATH[1]

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THERE are certain advantages in the use of a thermostatic air bath, especially for electrochemical measurements. These advantages include the low electrical conductivity of air and the elimination of the necessity of cleaning the outside of the apparatus. This cleaning is annoying in oil baths. This article describes such an air bath made from parts which were accessible and not very difficult to assemble.

The accompanying figures present a general description of the bath, but some observations may be in order. In Figure 1 the box covering the 10-in. fan blade is 15½ in. wide. It is closed, except for a hole in line with the center of the fan blade for an air intake, and an open bottom. The air moves into the bath proper through a 2-in. slit extending the width of the bath (25 in.), between the false bottom and the front of the bath. The approximate air flow, determined by experiment with suspended threads, is shown by the arrows.

The heater is made of No. 22 B. and S. gage resistance wire, having a total resistance of 82 ohms, wound on a piece of ¼-in. Transite (Johns-Manville Co.) 12 in. long and 6 in. wide. The heater is protected by a fuse made of Wood's metal.

The cooling coil consists of about 30 ft. of ¼-in. copper tubing wound back and forth to expose maximum surface. Because the available tap water is too warm to provide adequate cooling during the summer months, the water is kept at about 13°C. by recirculating it, by means of a pump, through a water cooler. The fan motor is mounted outside the bath to reduce vibration and exclude motor heat from the bath.

After trials with several different types and shapes of mercury-in-metal thermoregulators, one was made of ordinary steel tubing, 8 in. long, 1⁹/₁₆ in. o. d., with a wall thickness of 0.030 in., and holding 195 ml. of mercury. Attempts to clean ordinary steel tubes with acids followed by rinsing with water and acetone resulted in the appearance of a yellow film after the mercury was added. This film tended to float on the mercury

[1] Presented in part before the Chemistry Section of the Illinois State Academy of Science, May 7, 1952.

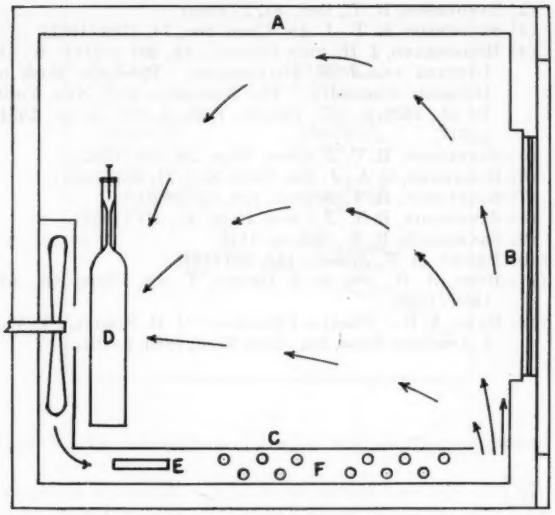

Figure 1. Air Bath

A, 30 in. × 30 in. × 30 in. wooden box, celotex-lined; *B*, door and cover; *C*, false bottom; *D*, thermoregulator without constant pressure device; *E*, heater; *F*, cooling coil.

surface and foul the contact with the iron wire. Finally, therefore, a length of open steel tubing was machined down to proper wall thickness, the inside polished with fine abrasives, the bottom and top pieces pressed in and welded; and then with no further cleaning, the mercury was added. The mercury was boiled during the filling to drive out dissolved and occluded air.

The regulator top is made of Pyrex glass which is cemented to the regulator and which has a metal cap with a finely threaded screw cemented to it. There is a flare in the capillary where the mercury contacts the iron wire, which allows variation in sensitivity. The mercury was cleaned in a mercurous nitrate-nitric acid column several times, pin-holed, and distilled three times, the last time in a nitrogen atmosphere; but after varying periods of time it still formed a film on cleaned glass. The inside of the capillary, therefore, was coated with General Electric DRI-FILM 9987 to decrease the tendency of mercury to form this film on glass. The regulator was designed to operate at 25°C. but could be made more versatile by a plunger attachment such as that described by Parks (*1*) and Yee and Davis (*2*). The regulator was given a thin coat of lacquer on the outside to prevent corrosion and the regulator supports were placed outside the bath with the suspending chains hung free of the bath to eliminate vibrational effects. The constant pressure device has been previously described (*3*).

The features of the control unit are shown in Figure 2 and the circuit is a modification of the one proposed by Beaver and Beaver (*4*).

This system will operate without the rectifier, but the resulting chatter of the relay is annoying. While circuits employing thyratron tubes directly (*5*) and thyratron tubes to trigger relays (*6*) have been described, the above arrangement also operates satisfactorily.

The relay is one made by the American Instrument Company (Bulletin No. 921) with the circuit modified as shown in Figure 2. The 110-v. heating circuit is controlled by a mercury switch so that corrosion of contacts is no problem.

The bath was operated over a period of months under a variety of room temperatures and atmospheric pressures, and temperature recordings were made. The cooling water ran continuously while the heater operated only when contact was not made in the thermoregulator. A typical set of results over a three-day period showed a temperature of 25.00° with an average deviation of ±0.05°.

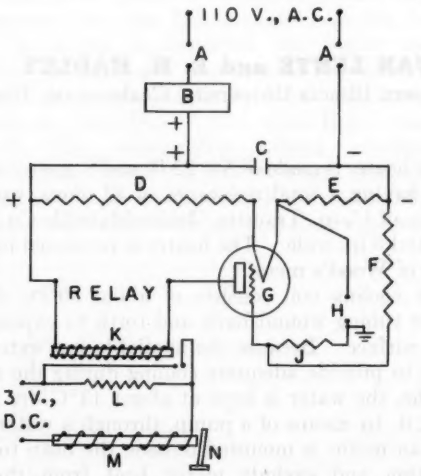

Figure 2. Control Unit and Relay

A, 0.5-amp. fuses; *B*, 150-v. selenium rectifier; *C*, 10 m.f.d., 600-v., d.-c. condenser; *D*, 332 ohms; *E*, 123 ohms; *F*, 4 megohms; *G*, 71 A-tube; *H*, thermoregulator; *J*, 0.4 megohm; *K*, 1006 ohms; *L*, 235 ohms; *M*, 6.8 ohms; *N*, arm carrying mercury switch for the 110 v., a.-c. heating unit.

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BUILDING A CHEMISTRY DEPARTMENT

I. The Undergraduate Curriculum

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In 1947 the author received an invitation to join the staff of the Illinois Institute of Technology, in order "to build an excellent chemistry department as rapidly as possible." The Institute had under construction a building which had originally been designed for the use of chemistry and biology but which, after some modification, was devoted solely to chemistry. This building and its facilities have been described elsewhere.[1] The present paper discusses the undergraduate curriculum, and subsequent papers will include discussion of the graduate program, educational policies, students and staff, teaching loads, the annual budget required, and the effect of sponsored research upon the educational program.

The philosophy in planning a new undergraduate curriculum was to graduate a man with a bachelor's degree who would be capable of doing research in a modern industrial laboratory without additional formal training. As it is impossible in a four-year curriculum to teach all of the many and various applications of chemistry to industrial practice, it was decided to confine the teaching to fundamentals.

The usual undergraduate curriculum has a minimum of one year each, with laboratory, of general, analytical, organic, and physical chemistry, with a year of college physics, mathematics through the calculus, and one additional course in chemistry. In the opinion of the writer, this is not sufficient chemistry and other science if the student is to terminate at the bachelor's level and go into industry, and the result is that a student who has chosen chemistry as a profession must go to graduate school for further training.

An undergraduate curriculum should give a man sufficient training in chemistry and other science to terminate at the bachelor's level and, at the same time, afford an opportunity for the exceptional student to go on to graduate school and specialize in his chosen branch of chemistry. This means that a properly trained B.S. in chemistry should be able to use the library intelligently, have sufficient knowledge of instruments as applied to chemical laboratory practice that he can use modern instruments with confidence, and above all be able to think for himself. In connection with his junior and senior courses, he should learn enough of the modern techniques of chemistry that he derive some personal satisfaction from his laboratory work in an industrial laboratory and not be just a "pair of hands" to a Ph.D.

At the same time, facility in oral and written communication and some knowledge of economics, history, and the humanities cannot be neglected in any bachelor's program. Unless a student is convinced that training in chemistry terminating at the B.S. level affords an attractive basis for remunerative employment and satisfactory working conditions, he will naturally turn to other fields. This is especially true of the student who, for financial or other reasons, cannot spend the additional time needed in a university to complete the work for the doctor's degree in chemistry.

During the academic year 1947–48 the problem of organizing an undergraduate curriculum was studied from the above point of view. The curriculum adopted at that time has been subject to continued faculty and student review. During the academic year 1951–52, the chemistry department staff conducted a series of discussions which included a review of the entire curriculum and of the content of each chemistry course and less detailed discussions with representatives from other departments in regard to their courses which were included in the chemistry curriculum. The general conclusion was that the curriculum was satisfactory but that certain specific improvements could be made.

In order to obtain the students' reaction to the curriculum, the I. I. T. Chapter of the A. C. S. Student Affiliates was asked to conduct a survey. A questionnaire was mailed out to some 70 students who had received the B.S. in chemistry from I. I. T. during the period 1948 to 1952, asking for a frank opinion of the entire curriculum, and posing the following questions:

(1) In your opinion, has your training enabled you to compete on an equal footing with B.S.'s in chemistry from other institutions in the United States?

(2) If your answer is *No*, please name the institution and what you consider the deficiencies in your program at I. I. T.

In all but one case, the answer to question (1) was *Yes*.

When the answers to the questionnaires had been received from the graduates, the undergraduates in the Student Affiliate group then conducted their own discussions.

As will be evident from the comments discussed

[1] Kilpatrick, M., in "Laboratory Design," H. S. Coleman, Editor, Reinhold Publishing Corp., New York, 1951, pp. 275–9.

below, the student and staff recommendations for changes were often in accord. So few changes from the earlier curriculum were made that it is considered unnecessary to itemize both the 1948 and 1953 curricula. The comments should be clear to the reader by reference to the revised curriculum shown in Table 1.

CURRICULUM

Freshman Year. Inorganic qualitative analysis is included in general chemistry (112).

Both staff and students recommended that algebra and trigonometry, which had been given in the first semester, be required for admission; that analytical geometry be given in the first semester, and calculus be started in the second semester. Educationally this has many advantages, but the recommendation was vetoed by the Institute curriculum committee on the grounds that the training in algebra and trigonometry in the Midwest high schools was inadequate.

The students pointed out that the two-semester course in technical drawing was designed for engineers and contained too much detailed work on drawing of "screws, nuts, and bolts," and did not use the metric system. The staff agreed with them that a one-semester course, emphasizing lettering, graphs and graphical representation of data, sketching, working drawings, and blueprint reading, should be substituted. This change has been made.

Sophomore Year. Both quantitative analysis and organic chemistry, taught in the sophomore year so that physical chemistry can precede the work of the senior year, made a heavy load for the sophomore. A one-semester, one-hour experimental course given by the chairman of the department was eliminated in 1950. The recommended change in mathematics would have decreased the load in the fourth semester.

Junior Year. After a thorough, one-semester course in organic qualitative analysis (331), the majors in chemistry spend two months of the spring semester on semimicro analysis for carbon, hydrogen, nitrogen, and organic functional groups, a month on the newer techniques of inorganic analysis, and a month on "chemistry under the microscope."

The students recommended that physical chemistry be a three-semester course with the elimination of electrochemistry in the senior year. This, however,

TABLE 1
Chemistry Curriculum (Revised) for 1953–54

		First semester			
Chem.	111	General Chemistry	4	4	5
Math.	101	Col. Algebra and Trigonometry	5	0	5
Engl.	101	Fundamentals	3	0	3
B.E.	101	Principles of Economics	3	0	3
P. E.	101	Physical Education	2	0	0
		Totals	17	4	16
		Second semester			
Chem.	112	General Chemistry	4	4	5
Math.	102	Anal. Geometry and Trigonometry	5	0	5
Engl.	102	Composition	3	0	3
B. E.	102	Principles of Economics	3	0	3
T. D.	108	Technical Drawing	1	5	2
P. E.	102	Physical Education	2	0	0
		Totals	18	9	18
		Third semester			
Chem.	223	Quantitative Analysis	2	8	4
Chem.	231	Organic Chemistry	3	6	5
Math.	201	Calculus	4	0	4
Phys.	201	General Physics	4	0	3
Phys.	205	Laboratory Physics	0	3	2
		Totals	13	17	18
		Fourth semester			
Chem.	232	Organic Chemistry	3	6	5
Math.	202	Calculus	4	0	4
Phys.	202	General Physics	4	0	3
Phys.	206	Laboratory Physics	0	3	2
P. S.	420	American Constitutional System	3	0	3
		Totals	14	9	17
		Fifth semester			
Chem.	341	Physical Chemistry	3	6	5
Chem.	331	Ident. Organic Compounds	2	8	4
Math.	410	Differential Equations	3	0	3
Germ.	101	Elementary German	3	0	3
Physics Elective			3	0	3
		Totals	14	14	18
		Sixth semester			
Chem.	342	Physical Chemistry	3	6	5
Chem.	323	Semimicro Analysis	2	8	4
Chem.	351	Chemical Literature	2	0	2
Germ.	102	Elementary German	3	0	3
Humanities Elective			3	0	3
		Totals	13	14	17
		Seventh semester			
Chem.	421	Instrumental Analysis	2	8	4
Chem.	411	Chemical Bonding and Structure	3	0	3
or					
Chem.	441	Electrochemistry	3	0	3
Germ.	211	Scientific German	2	0	2
Phys.	405	Quantum Theory of Struct. of Matter	3	0	3
or					
Bi.	441	Theoretical Biochemistry	3	0	3
General Elective			3	0	3
		Totals	13	8	15
		Eighth semester			
Chem.	413	Inorganic Chemistry	2	8	4
or					
Chem.	431	Organic Preparations	2	8	4
Germ.	212	Scientific German	2	0	2
Phys.	406	Quantum Theory of Struct. of Matter	3	0	3
or					
Bi.	442	Biochem. of Vitamins and Hormones	3	0	3
Liberal Studies Elective			3	0	3
General Elective			3	0	3
		Totals	13	8	15

The first number in the three columns gives the hours per week in the classroom, the second the hours per week in the laboratory or drafting room, and the third the semester hours of credit.

TABLE 2
Chemistry Teaching Option

First second, and third semesters: Same as in basic curriculum.
Fourth semester: Substitute Psych. 201, Introductory Psychology, for P. S. 420, American Constitutional System.

		Fifth semester			
Chem.	341	Physical Chemistry	3	6	5
Chem.	331	Ident. Organic Compounds	2	8	4
Math.	410	Differential Equations	3	0	3
Germ.	101	Elementary German	3	0	3
Educ.	301	Educational Psychology	3	0	3
		Totals	14	14	18
		Seventh semester			
Chem.	421	Instrumental Analysis	2	8	4
Chem.	411	Chemical Bonding and Structure	3	0	3
or					
Chem.	441	Electrochemistry	3	0	3
Germ.	211	Scientific German	2	0	2
Educ.	303	American Public Education	3	0	3
Educ.	317	Methods of High School Teaching	3	0	3
Educ.	310	Psychology of Adolescents	3	0	3
		Totals	16	8	18

		Sixth semester			
Chem.	342	Physical Chemistry	3	6	5
Chem.	323	Semimicro Analysis	2	8	4
Chem.	351	Chemical Literature	2	0	2
Germ.	102	Elementary German	3	0	3
Educ.	315	Secondary Education	3	0	3
		Totals	13	14	17
		Eighth semester			
Chem.	413	Inorganic Chemistry	2	8	4
or					
Chem.	431	Organic Preparations	2	8	4
Germ.	212	Scientific German	2	0	2
Physics Elective			3	0	3
P. S.	420	American Constitutional System	3	0	3
Educ.	408	Practice Teaching	0	10	5
		Totals	10	18	17

s impractical as the chemical and metallurgical engineers must complete physical chemistry by the end of he junior year.

In the opinion of the students, the course in chemical iterature (351) should reduce the emphasis on organic hemistry and spend some time on the less thoroughly ystematized fields of chemical physics, physical and norganic chemistry. Many students objected to ur one-year experiment of having a staff member rom the English department associated with the course, xplaining that although they recognized their weakess in written and oral expression, they felt that he English department should give a proper remedial ourse. Although this idea is basically a good one, to e successful it requires careful coordination and cooperation between the two staff members. A more easily ttainable solution was found by using a staff member rom the chemistry department who could play both oles, and in addition to improving the written English f the students, covered the literature in the various elds of chemistry.

Senior Year. In the earlier curriculum, inorganic hemistry (413) and organic preparations (431) were ffered with the emphasis on laboratory work, to give he students some training in glassblowing and in the echniques required in preparative chemistry. The udents suggested that the organic course should e brought up to the same standard as the inorganic, nd should include practical distillation with modern quipment, chromatography and extraction, and, in he lectures, greater emphasis on theory. Both staff nd students recommended that an additional semester f lectures on inorganic chemistry be added.

To meet these recommendations, a course in chemical bonding and structure (411) was added as an alternative to electrochemistry (441); and inorganic 413) and an improved organic course (431) were offered s alternatives in the eighth semester.

Instrumental analysis (421) is a course in the theory and application of instruments in chemical procedures, with analysis as a secondary objective. The philosophy is to teach that commercial instruments are not push-button machines which must be returned to the manufacturer for adjustment and repair. In addition to the formal experiments, each student is required to undertake a project, which usually begins in the library, is continued in the student machine shop, and is completed in the laboratory. For example, one year two students built and tested a workable magnetic susceptibility apparatus, and in the next year another student improved the apparatus, with the result that our Freund Instrumentation Laboratory now has another instrument for teaching and research. Although some of the experiments use homemade equipment, the student also works with the laboratory's double-beam infrared spectrometer, Beckman DU spectrophotometer, modern X-ray diffraction machine, polarographs, spectrograph, densitometer, and other modern instruments. The laboratory hopes, as funds become available, to acquire a mass spectrometer and a constant-temperature, constant-humidity room. In the meantime, instruction in the use of the mass spectrometer is provided by demonstrations in the well equipped laboratory of the Institute of Gas Technology located on our campus.

The students also suggested courses in report writing, speech, French, statistics, unit operations, radiochemistry, polymerization, and chemical thermodynamics. It was pointed out by the staff that—after all—we are required to limit ourselves to a four-year B.S. program! Unit operations, report writing, public speaking, and French are available as undergraduate electives; and statistics, chemical thermodynamics, radiochemistry, physical chemistry of high polymers, and a course on the colloidal state are available as graduate courses, and may be taken as electives by specially qualified seniors.

One obvious criticism of the curriculum is the paucity of free electives. Experience has shown us that although students might select suitable courses during the preregistration counseling period, it often happened that these courses were not available because of low registration or scheduling difficulties at the time of registration. The result was that courses were chosen on the basis of availability rather than suitability. To ensure that certain suitable courses would be available, alternative choices were provided instead of electives. The curriculum outlined in Table 1 is the minimum requirement and good students are encouraged to take additional courses during their senior year.

OPTIONS

The basic curriculum and the options outlined below meet the requirements of the American Chemical Society Committee on Professional Training.

Research Option. Only students of exceptional ability are permitted to enroll for this option. Permission is granted upon a written request to the chairman of the department and subsequent approval by the chemistry staff.

The research option is the basic curriculum in which eight semester hours of senior research (491) are substituted for the six semester hours of general electives in the seventh and eighth semesters and the project part of instrumental analysis (421). Senior research is also offered every summer.

Management Option. The management option is the basic curriculum in which 15 hours of approved business and economics courses are substituted for the general electives, and Physics 405–406 or Biology 441–442 in the seventh and eighth semesters.

Teaching Option. The teaching option involves the substitution of 24 hours of approved education and psychology courses in the basic curriculum as noted in Table 2. This program meets the present minimum requirements for education courses in Cook County and the State of Illinois.

The basic curriculum amounts to 134 semester hours with 59 taken in the chemistry department and a possible six of biochemistry in the biology department. The research option has 136 semester hours, with 67 in chemistry; the management option, 134 with 59 in chemistry; and the teaching option, 139 with 59 in chemistry.

The chemistry department staff is of the opinion that this curriculum provides training for a good chemist at the B.S. level, one who will be able to compete with any in the country. Evidence is already being provided by the approximately 100 graduates of the department since 1947, 30 per cent of whom have gone to graduate school at other institutions. Five have now received the Ph.D. degree, two are instructors in university chemistry departments; one fought off the coast of Korea and another did a tour of duty in the Chemical Corps before going on to graduate school. The others can be found in the laboratories of the Government and in industry in various capacities. Reports from professors in the other graduate schools are more than favorable, and in so far as we have been able to determine and compare, the chemistry students from I. I. T. show clearly the results of better-than-average training in the techniques of the laboratory.

The aim of the department is to turn out a quality product. Not all are from the same mold and there will be great differences, but if you have a sample we would like to hear about the defects as well as the good qualities so that we may improve the product. The product will depend greatly upon the starting material, and we are interested in receiving more and better material for processing.

EDGAR FAHS SMITH CENTENARY

AN EXHIBIT commemorating the centenary of the birth of Edgar Fahs Smith, who was born May 23, 1854, will be held in the Main Library of the University of Pennsylvania, 34th Street and Woodland Avenue, Philadelphia, Pennsylvania, from May 10 to 31, 1954. The late Professor Smith was three times President of the American Chemical Society and was a founder of the Divisions of Chemical Education and the History of Chemistry, as well as of the JOURNAL OF CHEMICAL EDUCATION. Among his numerous writings in the history of chemistry were "Old Chemistries," "The Life of Robert Hare," "Chemistry in America," and "Chemistry in Old Philadelphia." Following his death in 1928, his extensive library, devoted mainly to the history of chemistry, was presented to the University of Pennsylvania by his widow, the late Margie A. Smith, who afterward assured the maintenance and growth of the collection with a substantial endowment. The exhibit will draw upon the resources of the Smith Memorial Collection and will feature books, pictures, manuscripts, medals, apparatus, and other memorabilia associated with the life and career of Professor Smith. During the period of the exhibit, the Library will be open 8:45 A.M. to 10:00 P.M. Mondays through Fridays, 8:45 A.M. to 5:00 P.M. Saturdays and 2:00 to 6:00 P.M. Sundays.

FEDERAL SUPPORT OF BASIC RESEARCH AT A STATE UNIVERSITY[1]

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GERMANY, no doubt, led the world in physical and chemical research before World War I. Indications of this are the number of Nobel Prizes won, the number of students going there for advanced study in these fields, and the important papers in the scientific journals of the times. The reason certainly was not that Germany had the most liberal of governments, although this would have helped. Indeed, it was in spite of the government's militaristic propensities. Whatever its other faults were, however, imperial Germany poured money into advanced research in the universities. Industry did the same and the scholar was an honored member of society. The result was a great blossoming in all of the fields so supported. With defeat came a more liberal government but a decline in German scientific pre-eminence, very much in proportion to the decline in scientific support and the increase in support for science in this and other countries. The defeat after World War II, with its increased stringency and its loss of scientists before and after the war, by death and to other countries, has had its inevitable effect. Physical science will not return to its former pre-eminence in Germany until universities and other research institutions again receive the necessary financial support.

Russia provides a second fascinating case history. Under the Czars popular education as we know it in America was, of course, nonexistent; there were excellent technical schools where scholarly work was done. The revolution has brought an even worse government to power, but this government has recognized the need for technical education and the indications are that Russia is turning out more graduate engineers than we are. There is a lot of wishful thinking to the effect that doctrines like those of Lysenko and like the other bizarre theories about the so-called "Great October Revolution" somehow will magically nullify the great research efforts they are making. This just isn't so. Molecules have a way of ignoring the political opinions of experimenters. If the Russians have the wisdom to get their top intellects into the laboratory with proper facilities and then let them alone, they will get scientific results just as surely as if Russia were a great democracy. Most of what will now be said about state-supported Universities applies more or less equally to the private institutions.

American state universities vary greatly in quality, depending largely upon how much money gets spent on them. Intermittently they go through periods when some governing genius decides it is time to economize on the university and modernize the prisons. The period of stringency never lasts long but the damage does. Able professors get invited to competing institutions and are replaced by whoever is available. Unfortunately for the quality of education, there is no way to get rid of plodding mediocrities. The damage of a bad turnover in top personnel in a university is felt for thirty-five years—more than a generation. Since the top 10 to 15 per cent of the faculty make the difference between distinction and mediocrity, much of a university's quality depends on how long it has been since it last went through the wringer. More often than not, the period of stringency bites deeper into research than into any other part of the university program. In such periods, aid to research from outside sources cushions the blow substantially. Our state universities are frequently so short of funds that only a fraction of the best people with real talent for investigation are attracted to such fields.

Making the field of scientific research more attractive to the people who now go into business and other professions could greatly increase the number of scientific investigators, without seriously decreasing their quality. If continued too far, however, the quality of investigators attracted would eventually drop below the point at which the results produced would justify using them. Just where this point is, is a complicated problem and changes with circumstances. Although the initial cost of development of the first atomic bomb is estimated at about two billion dollars, we must measure this tremendous expenditure against the four billion dollars per year our recent Korean venture has cost us. Thus even such expensive research more than justifies itself as an economic measure if it buys us even a short interval of peace. This leaves out of account the priceless lives saved and the fact that the bomb ushered in the Atomic Age.

When one considers that scientific "know-how" is a lasting good and is superseded only by a deeper understanding of how operations should be carried out, it seems difficult to see how society can ever spend too much of its surplus in scientific research. A simple example shows how research has made the use of human muscles, in competition with machines, completely anachronistic. A hard-working, able-bodied man can throw 20 tons of coal over a 10-foot fence in a day. This corresponds to 400,000 foot-pounds

[1] Presented as part of a symposium on "Federal Support of Basic Research" at the 123rd Meeting of the American Chemical Society, Los Angeles, March, 1953.

of work. In six days he would do 2,400,000 foot-pounds of work. This is less than the 2,655,000 foot-pounds in a kilowatt hour which, when purchased in quantity, costs less than a penny. The only kind of power economically justifiable is that of machines. It has been observed that since oil was discovered about 90 years ago, the total use of power has increased about 1500 per cent and our national income has increased almost in exact proportion. In fact, the 5 horsepower operating per individual in the country is equivalent to about 40 slaves. These fruits of research almost completely shape our modern world. Even if one subscribes to the thesis that every bit of our surplus that is invested in research brings back more returns than any other possible use of it, many problems still remain. Thus fundamental research which in the long run benefits everyone almost equally still has to be done by individuals. On the other hand, certain practical investigations may have almost their sole value for the company using a particular process. On the theory that he who benefits should bear the expense, we clearly have two very different cases. Equity requires that the company—actually its customers—pay for the applied research and that fundamental research be paid for by the general public. High income taxes have depleted the number of people in this category able and willing to donate support for fundamental research. The only other source is government. Where the states can and will provide the necessary funds, it is better that they do so, since the university administrators are already responsible to the state and contracts can be more informal and, in general, there can be less red tape. Where the states can't or won't support fundamental research adequately, society will be better off if the federal government does it. According to my considered opinion, the federal agencies, supporting research, have done an outstanding job.

The University of Utah receives about two million dollars a year for research, in addition to what the state provides. About half of the two million goes to the Medical School; the rest goes largely to the physical sciences. Of this latter amount, about a quarter of a million is for research done under government contract off the campus. This involves business administration by the university and some technical supervision, but the staff doing most of the work are not resident at the university. Another sixth is for a restricted program on the campus, while the remainder is without restriction except that it be used for the projects for which it was originally granted. This latter money is as free from restrictions as are state funds. Thirty-one per cent overhead takes care of the University's expenditures. Fortunately, we are able to purchase necessary equipment from other sources. The quarterly progress reports, although they take some extra work, probably do us as much good as harm. We have not encountered any disposition on the part of those in charge of the government programs to interfere in any way with people at the university doing the actual research work.

The selection of people to receive research grants depends on the nature and documentation of the proposal and the past performance of the person seeking the grant. So far as my observations go, requests for grants are as equitably handled as one could reasonably expect. Undoubtedly some worthy requests have not been granted, while less promising ones may have been. This is humanly unavoidable. When one measures even the generous research grants of the services against the value and the cost of one more battleship or giant plane, it should be evident that not enough has been devoted to research.

There is one thing which both the universities and the supporting organizations must guard against. This is too swift a change in the amount of money devoted to research. If the government decides to lessen its support, it may be disastrous unless it tapers off slowly and allows the universities to liquidate their programs in an orderly manner. University officials must resist the natural tendency of state government officials to shift the whole burden of a reasonable-sized research program onto the federal government. This is not always easy but anything else may mean eventual ruin.

A natural, and I think desirable, move for the federal government would be to gather all the funds for support of fundamental research into a single agency, probably the National Science Foundation, and to leave the more applied aspects with the services. With careful administration our society would undoubtedly be much better off in the long run if the present comparatively generous federal research grants to universities were doubled. The only thing that would be better would be a reduction in federal taxes so that the state governments could make the grants themselves, if they would. In any case, it will be interesting to watch future developments. The best dollars society now spends are those which go into capable hands for fundamental research!

JOJOBA OIL, A LIQUID WAX, AND SOME OF ITS APPLICATIONS

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THE jojoba plant, *Simmondsia californica*, is unique, since it appears to be one of the few natives of the arid and often mountainous areas of North America that produces a fruit of potential economic importance. This evergreen shrub, found in Arizona, Lower California, and western Mexico, is eaten by browsing animals, and its fruit is used as food by various rodents. When mature, the fruit, which has a somewhat bitter taste, appears as a thin, brown, three-valved capsule containing a single nut or bean. The bean possesses a rough, reddish-brown, tightly adhering skin which contains a dark brown resinous material with an aromatic odor resembling that of propolis or bee glue. This material is soluble in acetone but insoluble both in the oil and in benzene so that it does not contaminate the oil when it is expressed or when it is extracted with benzene.

The beans used in the present work were picked in Arizona in 1942. Their characteristics, as well as those of their oil, were found to be similar to the characteristics reported by other investigators (*1, 2, 3, 4*) most of whose work has recently been summarized by Mirov (*5*). The smallest and largest of a group of 1000 beans, picked at random, weighed 0.1296 and 1.3003 g. respectively. Their moisture content was 4.1 per cent by both the toluene method and the oven moisture determination at 105°C. Extraction of the crushed beans with benzene for 100 hours resulted in a 45.2 per cent yield of an amber-colored oil with a mild, pleasant odor. The oil darkened on heating to 300°C., but when allowed to cool it began to lighten in color, and within two hours it was substantially colorless. The color had not darkened after two years, although some evidence of rancidity had developed in samples left open to the air.

The extracted oil had the following viscosity characteristics:[1]

Temp. in °F.	*Viscosity*	
	Centistokes	*SSU*
100	26.34	124.6
210	6.54	47.4

The viscosity index of the oil, therefore, is 172.

Various characteristics of the extracted oil were determined and are presented below in tabular form; all iodine numbers were determined by the Hanus method.

Density	$0.8638\ ^{25}_{25}$; $0.8613\ ^{25}_{4}$
N^{25}_{D}	1.4636
Iodine no.	80.82
Saponification no.	90.0
% Saponifiables	48.3
% Unsaponifiables	51.7
Iodine no. of saponifiables	80.2
Iodine no. of unsaponifiables	81.3

A sample of oil was dried 20 months over P_2O_5 without altering either the saponification or iodine numbers, but the refractive index was increased by eight in the fourth decimal place.

Saponification with alcoholic KOH, followed by precipitation through the addition of barium chloride, gave a solid mass containing the barium soaps and most of the alcohols when concentrated solutions were used. Acetone extraction of the solid mass and petroleum ether extraction of the aqueous portion when necessary yielded the free alcohols. Acidification of the residue from the acetone extraction followed by ether extraction yielded the free fatty acids.

The free alcohols and particularly the free acids from jojoba oil, like other fatty alcohols and acids, would find some applications in the free state, but the widest field of application is undoubtedly in some combined form, and some of their potential applications are listed below. In general they might be expected to find application in the lubrication, paint, ink, textile, rubber, plastics, metal-working, cosmetic, and many other industries, as well as in medicine. The fatty acids serve as intermediates in the preparation of long-chain alcohols, aldehydes, ketones, esters, amines, amides, nitriles, sulfated products, various metal soaps, etc., which find various applications as in disinfectants, surfactants, detergents, lubricants, driers, emulsifiers, resins, plasticizers, protective coatings, and corrosion inhibitors.

The alcohols may find application by themselves or as intermediates in the preparation of long-chain ethers, hydroxyethers, vinyl ethers, esters, sulfated products, etc., and in their various forms could be expected to find application as bases for various creams and ointments and in lubricants, surfactants, plasticizers, detergents, waxes, resins, emulsifiers, antifoamers, and in many other ways.

This potentially valuable oil appears to have received undeservedly little attention on a commercial basis. Ellis (*6*) used it as a factice in floor-covering ma-

[1] The author wishes to express his appreciation to the Swan-finch Oil Co. of Newark, N. J., in whose laboratories these viscosity measurements were made.

terials, while Flaxman (*7*) and Wells (*8*) have both reported its use as a sulfurized base for cutting oils. The author's patent completely describes a generally applicable rapid method of sulfurization as well as the product obtained from jojoba oil through its use, a product which surprisingly and unexpectedly contained almost 31 per cent of combined sulfur.

On the basis of the iodine number, jojoba oil also provided somewhat unexpected results on sulfation. Sulfated (often erroneously termed sulfonated) products have been derived from most of the more important and from many of the less important fatty oils of commerce. Some of these products have been known and used for almost a century and have found wide application in the textile industry in particular. Under various trade names they are used as surfactants for many purposes, including that of defatting. They are used as textile-softening agents and as lubricants for spinning operations. They find application as at least a part of the vehicle in many textile-treating agents such as dullers, weighters, and sizers, and they are used in calico printing and in dyeing where they form lakes and often act as fixing agents for certain types of dyes. Turkey Red Oil (sulfated castor oil) was so named when it was found that its use instead of olive oil in the production of Turkey Red (alizarin or Adrianople Red) from madder root drastically reduced both the complexity of and the length of time required for the operation.

Fatty Matter	*% SO_3*
Castor oil	16.7
Cottonseed oil	16.9
Rapeseed oil	16.8
Sperm oil	12.4
Jojoba oil	16.7
Jojoba saponifiables	16.8
Jojoba unsaponifiables	16.5

Jojoba oil, which is composed almost entirely of esters of 11-eicosenoic and 13-docosenoic acids and 11-eicosenol and 13-docosenol, according to previous investigators (*2*, *4*), should yield sulfurized and sulfated products containing approximately the same amount of combined sulfur or acid sulfate radical as does sperm oil. The sulfation process used consisted of adding twice the theoretical quantity of concentrated sulfuric acid (98 per cent), over a period of two hours, to the oil, which was constantly agitated and kept at a temperature of 0°C. by the direct addition of dry ice. The mixture was then neutralized at not over 5°C. and salted out; the product contained about 60 per cent of the sulfated jojoba oil. Castor, cottonseed, rapeseed, and sperm oils and jojoba saponifiables and unsaponifiables were all subjected to the same process of sulfation for comparative results. In all cases the products were analyzed for SO_3 by the standard hydrolysis method, and the results, based on the sulfated fatty matter, are given in the table on this page.

In order to meet all his customers' requirements, the sulfated oil producer often finds it necessary to supply oils which are more soluble or emulsifiable than those produced directly by sulfation. To obtain the desired results, the batch, usually before salting out, is treated with dilute sulfuric acid at a moderate temperature. This treatment hydrolyzes the ester linkages with little attack on the sulfate linkages so that subsequent neutralization causes formation of soaps of the hydrolyzed sulfated fatty acids. It is well known that, according to the fatty content, such treatment liberates about one per cent of free fatty acid per hour for each per cent of free sulfuric acid present in the case of most oils and about 0.8 per cent free fatty acid from sulfated castor oil.

Mixtures were made up containing 60 per cent sulfated jojoba oil and 1, 2, and 4 per cent free sulfuric acid. Similar mixtures were also prepared from sulfated castor oil and sulfated rapeseed oil, and all mixtures were held at 40°C. for four hours, samples being taken from each every hour for analysis. The average results of the analyses showed that sulfated rapeseed oil hydrolyzed to yield 0.95 per cent free fatty acid per hour for each per cent free sulfuric acid present, while the sulfated castor oil yielded 0.78 per cent free fatty acid, and the sulfated jojoba oil yielded 0.76 per cent free fatty acid per hour per each per cent free sulfuric acid present.

In addition to its potential value as a raw material for sulfurized and sulfated oils, jojoba oil is probably the best and perhaps the only source of C_{20} and C_{22} alcohols, and by variations of known procedures it may be converted to a large number of other useful products.

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INDUSTRIAL ADVERTISING AS A SOURCE OF INFORMATION

W. G. KESSEL
Indiana State Teachers College, Terre Haute, Indiana

"TODAY'S news of the chemical world likely to influence the happenings of tomorrow." This statement has been seen at the head of a column called conCENtrates in *Chemical and Engineering News* for some time. Any consideration of advertising in the field of chemistry will emphasize this idea that the manufacturing concerns hope to "influence the happenings of tomorrow." In order to accomplish this end the advertising man and the public relations writer are continually alert to give the reader concise, specific, revealing ideas and facts concerning their products and processes. Therefore the chemistry teacher would be remiss in his field if he did not take advantage of the great volume of advertising and public relations information available.

This article is the fourth of a series published in THIS JOURNAL.[1]

Vannevar Bush, in addressing the Twenty-Third Annual Scientific Assembly of the Medical Society of the District of Columbia, issued a warning against overspecialization in the fields of science and the consequent development of a tower of Babel, an unintelligent jargon which only the initiate could understand. The teacher is very much aware of this situation, for daily questions about new products, processes, and terms are brought to his attention, even words, phrases, and names that are not to be found in the "new" texts. His only source is the current journals and literature and the aids given by the public relations and advertising departments.

Nowhere can the teacher find a better, more thorough discussion of certain topics than in the trade literature.

"The Importance of U. S. Patent System" is the result of seminars on "What Inventions Mean to You" held by the Patents Committee of the National Association of Manufacturers from 1948 to 1952. This is an excellent treatise on the patent system in terms of its development and principles and its contributions to us. During these past few years vocational guidance has increased in scope and a multitude of fine publications have been developed for the teacher-counselor. The NAM's "Your Opportunities in Science" is very enlightening for the junior- or senior-high pupil.

Others might be used as specific examples of the contributions made by the advertising and public relations fields to the literature of chemistry. However, the best procedure would be to examine the offerings in the list following, which with few exceptions can be procured by writing for them on your letterhead.

Topic	Company Address
The Chemistry and Application of Acrylonitrite in Manufacturing of Adhesives	American Cyanamid Co., 30 Rockefeller Plaza, New York 20, New York
Alcoa's East St. Louis Research Laboratory	Aluminum Co. of America, Pittsburgh, Pa.
Aluminum A B C's	Technical Service, Reynolds Metals Co., 2500 East 3rd, Louisville, Kentucky
Aluminum Bulletin, Spring 1952	Aluminum Association, 420 Lexington Avenue, New York, New York
Rapid Identification of Some Metals and Alloys (Spot-Testing Analysis)	Development and Research Division, International Nickel Co., New York 5, New York
The Atom Produces a New Industrial Tool	Nuclear Research and Development Co., 1049 Sutter Avenue, St. Louis, Missouri
The Care and Use of Balances	Christian Becker Division of Torsion Balance Co., Clifton, New Jersey
The Inside Story of Dry Batteries	National Carbon Co., Division of Union Carbide & Carbon Co., 30 East 42nd Street, New York 17, New York
What It Takes to Make Your Car	Automobile Manufacturers Association, 320 New Center Building, Detroit 2, Michigan
Celite—The Story of Diatomite	Johns-Manville, 22 East 40th Street, New York 16, New York
A Trip through the Lone Star Cement Mill at Greencastle, Indiana	Lone Star Cement Co., Greencastle, Ind.
Chemicals in Foods: Spring 1952 issue of "Progress Through Research"	General Mills, Inc., 400 2nd Avenue S., Minneapolis, Minnesota
Chemicals from Coal	Carbide and Carbon Chemicals Corp., 30 East 42nd Street, New York 17, New York
The Chemical Profession	American Chemical Society, 1155 16th Street, N.W., Washington 6, D. C.
Chlorophyll, 1953	American Chlorophyll Division, Strong Cobb and Co., Inc., Lake Worth, Florida
CO_2 and Dry Ice, Industrial Uses	Liquid Carbonic Corp., 3100 S. Kedzie Avenue, Chicago 23, Illinois
Copper, 150 Years in the Industry	Revere Copper and Brass, Inc., 230 Park Avenue, New York 17, New York

[1] The previous articles on this subject appeared in **21**, 437 (1944); **25**, 222 (1948); and **28**, 383 (1951).

Romantic Copper	Copper and Brass Research Assoc., 420 Lexington Avenue, New York 17, New York
Copper Naphthenate	Witco Chemical Co. 245 Madison Avenue, New York 17, New York
Synthetic Optical Crystals	Harshaw Chemical Co., 1945 East 97th Street, Cleveland, Ohio
Dacron—Polyester Fiber	E. I. du Pont de Nemours & Co., Inc., Nylon Division, Wilmington, Delaware
Demineralization of Saline Waters	Office Secretary, U. S. Department of Interior, Saline Water Program, Washington 25, D. C.
Detergency Evaluation	Monsanto Chemical Co., 1704 South 2nd Street, St. Louis 4, Missouri
Dowcide Preservatives (fungicides and germicides)	Dow Chemical Co., Department D.P.-12, Midland, Michigan
Dynel	Textile Fibers Dept., Chemical Division, Carbide and Carbon Chemicals Co., 30 East 42nd Street, New York 17, New York
The Edison Effect	Thomas Alva Edison Foundation, Main at Lakeside, West Orange, New Jersey
Can I Be an Engineer?	G. P. O'Connell, Education Relations Secretary, Public Relations Department, General Motors Corp., 3044 West Grand Boulevard, Detroit 2, Michigan
Ethylene Oxide and Ethylene Glycol by the Shell Process	The Lummus Co., 385 Madison Avenue, New York 17, New York
Esters	Carbide and Carbon Chemical Co., 30 East 42nd Street, New York 17, New York
Fibers, Man-made	Textile Fibers Department, E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware
Modern Fuel Oils and the Application of Additives	E. F. Drew & Co., Inc., 15 East 28th Street, New York 10, New York
Fluorescent Lamps	Westinghouse Electric Corp., Lamp Division, Bloomfield, New Jersey
Fluorescent Pigments	Rhode Island Labs., Inc., West Warwick, Rhode Island
The Story of Gas	American Gas Association, 420 Lexington Avenue, New York 17, New York
The Story of Handmade Glass	Imperial Glass Co., Bellaire, Ohio
Laboratory Glassblowing with Pyrex Brand Glasses	Laboratory and Pharmaceutical Sales Department, Corning Glass Works, Corning, New York
Hormones — The Chemical Bridge for Life	Drexel Institute, Philadelphia, Pennsylvania
Iodine, Its Properties and Technical Applications	Chilean Iodine Educational Bureau, Inc., 120 Broadway, New York 5, New York
Lantern Slides and How to Make Them	Educational Sales Division, Bausch & Lomb Optical Co., 786 St. Paul Street, Rochester 2, New York
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The Story of Lindane	California Spray Chemical Corp., Richmond, California
Industry Looks at Lithium	Foote Prints, Vol. 25, No. 1, Foote Mineral Co., 18 West Chelten Avenue, Philadelphia 44, Pa.
The Eight Precious Metals	International Nickel Co., 67 Wall Street, New York 5, New York
Methanol	Commercial Solvents Corp., 260 Madison Avenue, New York 16, New York
Methocel	Dow Chemical Co., Midland, Michigan
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Linde-Fraenkl Process (low-cost tonnage oxygen production)	Blaw-Knox Construction Co., Chemical Plants Division, P.O. Box 778, Pittsburgh 30, Pa.
Precision—A Measure of Progress	Department of Public Relations, General Motors, Detroit 2, Michigan
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Phosphoric Acid, The Manufacture of, by the Wet Process	The Dorr Co., Barry Place, Stamford, Connecticut
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pH Indicator Chart	Eastman Organic Chemicals Dept., Distillation Products Inc., Rochester 3, New York
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Products and Processes	Union Carbide & Carbon Corp., 30 East 42nd Street, New York 17, New York
Rayon and Acetate Information	American Viscose Co., 350 5th Avenue, New York 1, New York

Industry and Government Research	National Association of Manufacturers, 14 West 49th Street, New York 20, New York
Research, A Case Book of Calva	J. B. Calva & Co., Minneapolis 1, Minnesota
The Story of Research	E. I. du Pont de Nemours & Co., Inc., Public Relations Department, Wilmington, Delaware
Battelle Memorial Institute (research work)	Battelle Memorial Institute, 505 King Avenue, Columbus 1, Ohio
Resources (reprint, *The Atlantic Monthly*, June, 1952)	Standard Oil Co. of New Jersey, Room 1626, 30 Rockefeller Plaza, New York 20, New York
Riboflavin	Commercial Solvents Corp., 260 Madison Avenue, New York 16, New York
Natural Rubber and You	Natural Rubber Bureau, 1631 K Street, N.W., Washington 6, D. C.
A Visit to a Synthetic Rubber Plant	Public Relations Dept., U. S. Rubber Co., 1230 Avenue of Americas, New York 20, New York
Indianapolis Plant of U. S. Rubber	U. S Rubber Co., 649 Georgia Street, Indianapolis 6, Indiana
The Story of Safety	Public Relations Dept., E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware
Rock Salt Mining	International Salt Co., Inc., Scranton, Pennsylvania
Your Opportunities in Science	National Association of Manufacturers, 14 West 49th Street, New York 20, New York
Sequesterene	Alrose Chemical Co., Box 1294, Providence 1, Rhode Island
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Sodium Dispersions	E. I. du Pont de Nemours & Co., Inc., Electrochemicals Dept., Wilmington 99, Delaware
Sorbitol Story	Atlas Powder Co., Wilmington, Delaware
The Story of Cane Sugar	American Sugar Refining Co., 120 Wall Street, New York 5, New York
Sucrose Utilization	Sugar Research Foundation Inc., Report #7, L. F. Wigging, 52 Wall Street, New York 5, New York
Surface-Active Agents	Onyx Oil & Chemical Co., Indiana Division, Warren & Morris Streets, Jersey City 2, New Jersey
The Mighty Tin Can	Weirton Steel Co., Weirton, West Virginia
Transistors, Today and Tomorrow	Radio Corporation of America, RCA Building, 30 Rockefeller Plaza, New York 26, New York
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Vanadium, Mesa Miracle	U. S. Vanadium Co., 30 East 42nd Street, New York 17, New York
High Vacuum Apparatus Bulletin 10	Central Scientific Co., 1700 Irving Park Road, Chicago 13, Illinois
Water Conditioning Data Book	Permutit Co., 330 West 42nd Street, New York 36, New York
Water and Liquid Treatment by Ion Exchange	Illinois Water Treatment Co., 899 Cedar Street, Rockford, Illinois
Water Treatment, Nalco Ion Exchange Materials	National Aluminate Co., Chicago 38, Illinois
The Story of Wedgwood	Josiah Wedgwood & Sons, Ltd., 25 East 54th Street, New York 22, New York
This Thing Called Yeast	Standard Brands, Inc., 595 Madison Avenue, New York 22, New York
Zinc, in the World of Things	New Jersey Zinc Co., 160 Front Street, New York 38, New York
The Zinc Industry, a Mine to Market Outline	American Zinc Institute, 60 East 42nd Street, New York 17, New York
Properties and Prices of TAM Zirconium Metal	Titanium Alloy Mfg. Division, National Lead Co., 111 Broadway, New York 6, New York

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FREDERICK BELDING POWER, MOST DISTINGUISHED AMERICAN PHYTOCHEMIST

MAX PHILLIPS
U. S. Department of Agriculture, Washington, D. C.

THE year 1953 marked the one hundredth anniversary of the birth of Frederick Belding Power, the most distinguished investigator in the field of phytochemistry that this country has produced. The large number of original investigations conducted for over half a century for the purpose of unraveling the complex chemical mixtures that are plants, separating them into their constituent chemical compounds, identifying them, and, where necessary, determining their structural or constitutional formulas, has made the name of Frederick Belding Power famous in the annals of chemical literature the world over.

He was born on March 4, 1853, in Hudson, New York, the son of Thomas and Caroline Belding Power. He was a descendant of John Power, who migrated from England in the seventeenth century and settled in Providence, Rhode Island.[1] His early education was obtained at a private school and at the Hudson Academy. He graduated with honors from the Philadelphia College of Pharmacy in 1874, in the same class with his lifelong friend Henry S. Wellcome. In 1876 he decided he would carry out his long-cherished plan of completing his chemical and pharmaceutical education in Germany and matriculated at the University of Strassburg, and received the Ph.D. degree in 1880. In those days the faculty at Strassburg included such men as Fittig, Friedrich Rose, and Baeyer in chemistry, Kund in physics, Flückiger in pharmacognosy, Du Bary in botany, and Schmiedeberg in pharmacology. His favorite professor was Flückiger, who made him his private assistant in 1879–80.

EARLY WORK

While a student at the University of Strassburg, Power published seven articles dealing with such subjects as the resin of Podophyllum, emetine, and the constituents of peppermint oil and of the rhizome of *Asarum canadense*. For his investigations on the resin of Podophyllum, the American Pharmaceutical Association awarded him the Ebert prize in 1877.

On his return to America in 1880 he was appointed professor of analytical chemistry at the Philadelphia College of Pharmacy, he being the first to hold that chair. He also had charge of the chemical laboratory. He retained this position until 1883. It was during this period that, in collaboration with Dr. Frederick Hoffman, he published a book entitled "A Manual of Chemical Analysis," which was prepared primarily for students of pharmacy.

In 1883 he accepted an offer tendered by President Bascom of the University of Wisconsin to organize the Wisconsin School of Pharmacy with the titles of dean and professor. He gave instructions in materia medica and in pharmaceutical chemistry. In recognition of this service and in commemoration of the twenty-fifth anniversary of the founding of its School of Pharmacy, the University of Wisconsin conferred upon Power, in 1908, the honorary degree of Doctor of Laws.

During the nine years when Power was professor at the university of Wisconsin, he conducted original phytochemical investigations on essential oils, alkaloids, and other constituents of several drug plants. In 1884 he translated into English F. A. Flückiger's monograph "Die Chinarinden" and in 1887 F. A. Flückiger and A. Tschirch's book, "Die Grundlagen der Pharmacognosie."

In 1892 Power resigned his academic position at the University of Wisconsin in order to become scientific director of the newly established chemical laboratories of Fritzsche Brothers at Passaic, New Jersey, which were devoted to research on essential oils and fine chemicals. It was during this period that many of his well-known researches on essential oils were conducted. The results of his researches on the essential oils of American peppermint, bay, cloves, wintergreen, sweet birch, sassafras bark, sassafras leaves, and others were submitted in a series of articles, which were published in the *Pharmazeutische Rundschau* and in the *Pharmaceutical Review*.

ESSENTIAL OILS

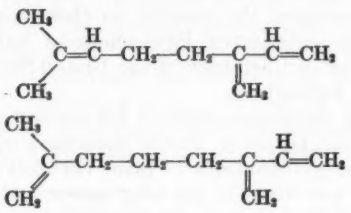
While it is not possible in a short paper to give an extended review of Power's chemical investigations of essential oils, his work on the constituents of oil of bay, because of its unusual scientific interest, deserves more than passing mention.

A discussion had arisen respecting the solubility in ethanol of the oil of bay, as distilled from the leaves of *Myrica acris* DC. The pharmacopoeia stated that the oil was soluble in an equal weight of ethanol. However, some observers contended that it afforded a turbid solution and that accordingly the statement in the pharmacopoeia was incorrect. It had subsequently been observed that the freshly distilled oil does, in fact, yield a clear solution with 90 per cent ethanol but when kept for some time, its solubility in this so

[1] "The National Cyclopaedia of American Biography," James T. White and Co., New York, 1940, Vol. 28, p. 461.

vent becomes impaired. In order to determine the cause of this change, Dr. Power subjected the oil to a complete chemical examination.[2]

The oil was separated into a neutral and a phenolic fraction, and in the latter eugenol and chavicol (*p*-allyl phenol) were identified. From the neutral fraction, in addition to citral and the ethers methyl chavicol and methyl eugenol, two hydrocarbon fractions were isolated. One of these was identified as phellandrene, and the other, which was optically inactive, was shown to be a so-called olefinic terpene, an open-chain hydrocarbon whose composition could be represented by the empirical formula $C_{10}H_{16}$. This hydrocarbon was found to have a density and molecular refraction lower than that of the ordinary terpenes. It contained three ethylenic linkages and was designated *myrcene*, with reference to its source. It was the first known representative of the so-called olefinic terpenes to have been isolated from a plant or plant product. It was shown that the constitution of myrcene could be expressed by one of the following formulas:

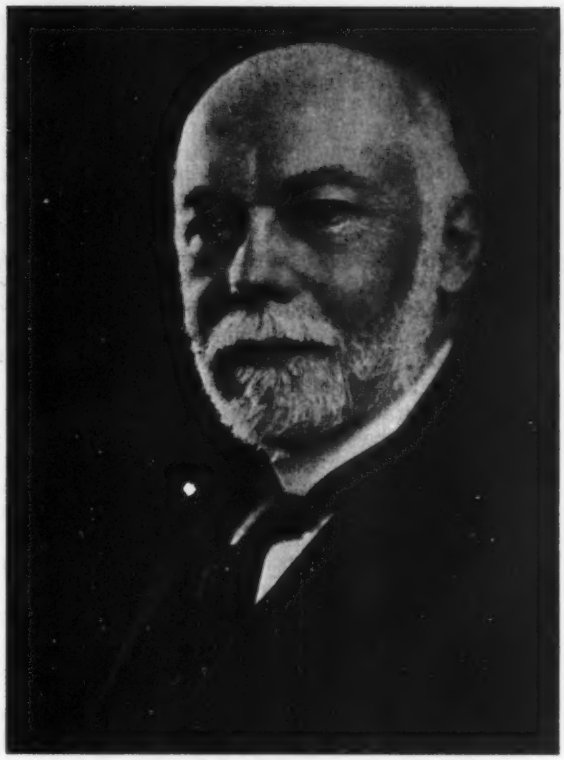


Myrcene readily polymerizes when subjected to distillation under ordinary pressure or when exposed to the air for some time, with the formation of a viscid product sparingly soluble in alcohol. This tendency of myrcene to polymerize accounts for the apparent discrepancies in the statement respecting the solubility of oil of bay in alcohol.

The isolation of the olefinic terpene myrcene was, at first, of scientific interest only. Later,[3] however, it assumed added significance in connection with the production of synthetic rubber. This is one of the many examples known to the student of the history of chemistry in which a discovery considered at first as being only of purely scientific or academic interest later became of considerable practical importance.

TO ENGLAND

In 1896 Henry S. Wellcome, Power's classmate and lifelong friend, established the Wellcome Chemical Research Laboratories in the central part of London, and he appointed Power director of that institution. The period of eighteen and a half years during which he was director of the Wellcome Chemical Research Laboratories was the most productive one of his life. He was in a position in which he could devote himself exclusively to phytochemical research and he was provided with adequate facilities and with a staff of highly trained chemists. Seventy-five papers of which Power was either the sole author or coauthor were published in various scientific journals, principally in the *Journal* of the London Chemical Society, while he was director of the Wellcome Chemical Research Laboratories. These papers constitute a record of accomplishment in phytochemical investigations that is almost without parallel. It is perhaps not too much to say that only those who have themselves worked in this field of investigations can fully appreciate how difficult and involved, how patience-taxing and exacting, and how time consuming is such work. It must be pointed out that Dr. Power was not only an accomplished scientist but also a master of the organic chemist's art.



Frederick Belding Power

Power's investigations and papers have a certain thoroughness, maturity, and finish, both in subject matter and in form. It has been truly said of him that "he possessed that peculiar faculty of exhausting each subject which he took up."[4]

Power had an excellent command of the English language and his papers, prepared with meticulous care, are noted for their clearness, precision, and polished literary style.

It is not the intention of the writer to give a review

[2] POWER, F. B., AND C. KLEBER, *Pharm. Rundschau* (New York), **13**, 60–3 (1895).

[3] OSTROMYSLENSKI, I. I., AND F. F. KOSHELEV, *J. Russ. Phys. Chem. Soc.*, **47**, 1928–31 (1915).

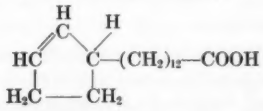
[4] GRIFFITH, L., *Am. J. Pharm.*, **96**, 601–14 (1924).

of all the various scientific papers published by Power and his associates during the time in which he was director of the Wellcome Chemical Research Laboratories. Only a brief account of some of them can be presented here.

CHAULMOOGRA OIL

The fatty oil known as chaulmoogra oil, which is obtained from the seeds of the plant *Taraktogenos kurzii* King, has been used in the treatment of leprosy and other skin diseases, and is the therapeutic agent regarded by some as a specific for leprosy. A complete chemical examination of chaulmoogra oil by Power and his associates[5] showed that its composition is entirely different from that of any other fat or fatty oil. Its chief constituents, to which its special therapeutic properties may be attributed, are glyceryl esters of acids of an entirely new type. These acids are optically active and have a cyclic structure; their composition is represented by the general formula $C_nH_{2n-4}O_2$. The composition of the acid present in the oil in the largest proportion is represented by the empirical formula $C_{18}H_{32}O_2$ and was designated chaulmoogric acid.

Chaulmoogric acid, although isomeric with linolic acid, combines with only two atomic proportions of bromine or iodine, and therefore has but one double bond, and it must contain in its structure a closed carbon ring. It was definitely established that it is a cyclopentene derivative, and that its constitution can be represented by the following structural formula:



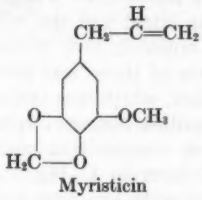
The other optically active acid present in chaulmoogra oil, termed hydnocarpic acid, was found to have a structure similar to that of chaulmoogric acid, and differs from it only by containing ten methylene groups in the aliphatic side chain instead of twelve.

NUTMEG

Nutmeg, a product of the East Indies, is used as a drug and as a condiment. When taken in considerable quantity, nutmeg possesses narcotic properties, although in the quantities ordinarily used as a condiment or flavoring agent it may be regarded as perfectly harmless.

The essential oil of nutmeg, to which its physiological properties may be attributed, was investigated by Power and Salway[6] and was found to be of very complex composition. It was found to contain pinene, camphene, dipentene, eugenol, iso-eugenol, linalool, borneol, terpineol, geraniol, safrole, myristicin, and formic, acetic, butyric, octoic, and myristic acids.

The physiological properties of nutmeg were found to be due to myristicin, $C_{11}H_{12}O_3$, which is 3-methoxy-4,5-methylenedioxy-1-allylbenzene.



Myristicin

Owing to conditions resulting from the outbreak of the first World War in 1914, there was a complete interruption of Power's research work at the Wellcome Chemical Research Laboratories, and he accordingly returned to the United States. He had then reached the age at which most men are content to seek rest in retirement. This, however, was not the case with him. In 1915, at the age of 62, he made a fresh start, and he accepted the position as chemist-in-charge of the newly constituted Phytochemical Laboratory of the Bureau of Chemistry of the United States Department of Agriculture.

During the eleven years of his connection with the Bureau of Chemistry, Power succeeded in making as important contributions to plant chemistry as he had done at any time of his long career. He published papers on the odorous constituents of apples, grapes, and peaches; on *Ilex vomitoria* as a native source of caffeine; on the chemical examination of the tubers of *Cyperus esculentus;* and on the nonvolatile and volatile constituents of the cotton plant.

COTTON

The investigation on the volatile constituents of the cotton plant was undertaken for the following reasons. It had been observed by entomologists that the cotton plant possesses a specific attraction for the boll weevil and it had been presumed that this was due to the emanation of some volatile substance that attracts the insects. It was considered that if the odorous substance could be isolated and identified, it might be possible to produce it synthetically and to use it to attract the insects to a poisoned bait.

The concentrated distillate obtained by distillation of the cotton plant with steam, which represented all its odorous and volatile constituents, was found to contain the following substances: methyl and amyl alcohols, acetaldehyde, vanillin, a phenol (possibly *m*-cresol), an optically inactive dicyclic sesquiterpene, an optically active tricyclic sesquiterpene, formic, acetic, and caproic acids, ammonia, and trimethylamine. Both ammonia and trimethylamine were found to be emanations from the living cotton plant.[7]

[5] POWER, F. B., AND F. H. GORNALL, *J. Chem. Soc.*, **85**, 838–61 (1904); BARROWCLIFF, M., AND F. B. POWER, *ibid.*, **91**, 557–78 (1907).

[6] POWER, F. B., AND A. H. SALWAY, *J. Chem. Soc.*, **91**, 2037–58 (1907); *ibid.*, **93**, 1653–9 (1908); *Am. J. Pharm.*, **80**, 563–80 (1908).

[7] POWER, F. B., AND V. K. CHESNUT, *J. Am. Chem. Soc.*, **47**, 1751–74 (1925).

In point of completeness Power considered his research on the volatile and nonvolatile constituents of the cotton plant, which was his last laboratory investigation, as his most finished piece of work.

The writer considers it a great privilege to have known Dr. Power during the last eight years of his life, when he was chemist-in-charge of the Phytochemical Laboratory at the Bureau of Chemistry. It was always an inspiration to visit his laboratory and observe how he conducted various chemical operations. Without the aid of the more modern tools of the chemist he was able to isolate and identify plant constituents, even when they were present in the minutest amounts. Only those who have themselves labored in the field of phytochemistry can fully appreciate how difficult, how patience-taxing is such work.

It must also be emphasized that Power was not the long-distance type of research director, that is, one who directs or attempts to direct chemical investigations from an office desk. The writer gained the impression that he loved laboratory work and did not consider it beneath his dignity to carry out with his own hands even the simplest chemical operations—operations which at the Wellcome Chemical Research Laboratories he could have had his assistants do for him.

Dr. Carl L. Alsberg, who was Chief of the Bureau of Chemistry at the time when Power was connected with that institution, had this to say about him:[8]

> It was not my privilege to know Dr. Power until after his return from London. From that time until the summer of 1921, I was closely associated with him. I came to appreciate his encyclopedic knowledge; his mastery of the technic of the organic chemist; his unerring instinct for the conditions under which a reaction or a process could be made to go, no doubt, the subconscious manifestation of a vast experience; his thoroughness and conscientiousness which made him incapable of presenting anything but sound work, matured and finished, both in subject matter and in form. I observed his unfailing kindness and courtesy to all the research workers of the Bureau of Chemistry who sought his advice. He soon became one of the strongest influences in the bureau for fostering that scholarship and research spirit which, under pressure for immediate and practical results, so easily perishes in industrial and research organizations.

Power received many honors and awards during his long scientific career.[9] He was awarded thrice the Ebert Prize of the American Pharmaceutical Association, in 1877, 1903, and 1907, the last jointly with Frank Tutin. Gold medals were conferred upon him at the St. Louis International Exhibition of 1904, at the Milan Exhibition of 1906, at the Franco-British Exhibition of 1906 in London, and at the Turin Exhibition of 1911. In 1913 the Chemical and Linnaean Societies and Pharmaceutical Society of Great Britain jointly awarded him the Hanbury Gold Medal in recognition of his researches in the natural history and chemistry of drugs, a distinction only once previously bestowed upon an American. In 1921 he received a gold medal, bearing his profile in relief, from his friend Henry

Medal Given to Power by Henry S. Wellcome

S. Wellcome "in recognition of his distinguished services to science during 18½ years as Director of the Wellcome Chemical Research Laboratories, London."[4] In 1922 he was awarded the Flückiger Gold Medal by the Swiss Pharmaceutical Society and in 1924 he was elected a member of the National Academy of Sciences.

The last year of his life was devoted to the collection of material and writing of a book on phytochemistry. It was to have been a comprehensive two-volume treatise upon this subject. Unfortunately, he did not live long enough to complete this work. He died in Washington, D.C., on March 26, 1927, and his remains were buried at his birthplace in Hudson, New York.

[8] ALSBERG, C. L., *Ind. Eng. Chem.*, **18**, 103 (1926).

[9] BROWNE, C. A., *J. Assoc. Offic. Agr. Chemists*, **11**, No. 2, V (1928).

AN INDUSTRIAL INSTRUMENTATION TEACHING AID[1]

COLEMAN J. MAJOR
State University of Iowa, Iowa City, Iowa

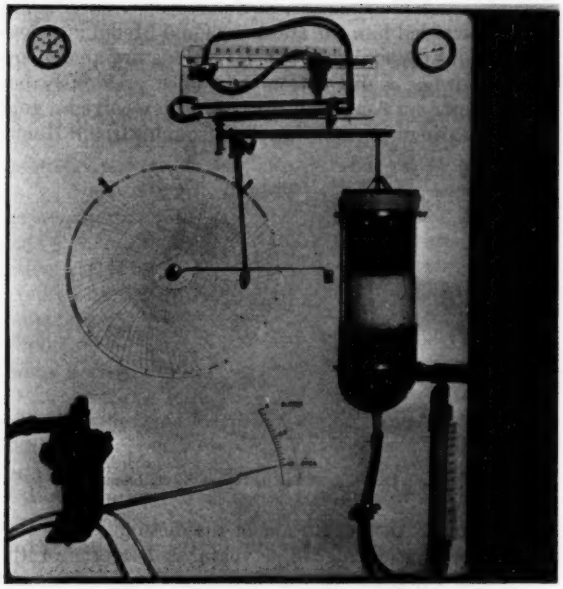


Figure 1. Instrumentation Teaching Aid

THE teaching of the fundamentals of industrial instrumentation is greatly facilitated by demonstrations of control instruments in actual operation. Commercial controllers may be used for classroom demonstration purposes but the chief disadvantages of these instruments are that they are costly and that they are somewhat too complicated for beginning students to understand.

The teaching aid developed by the author is relatively inexpensive to construct and offers an excellent means of demonstrating the fundamentals of industrial pneumatic instrumentation. Because all of the working parts are exposed on the panel, the student is able to observe how each part functions throughout the control period. The teaching aid may be used for lecture demonstrations in the classroom or it may be used by students in the laboratory for carrying out various instrumentation experiments.

Apparatus. A photograph of the apparatus is shown in Figure 1. A schematic diagram of the apparatus is

[1] Presented at the Symposium on Process Instrumentation at the 124th Meeting of the American Chemical Society, Chicago, September, 1953.

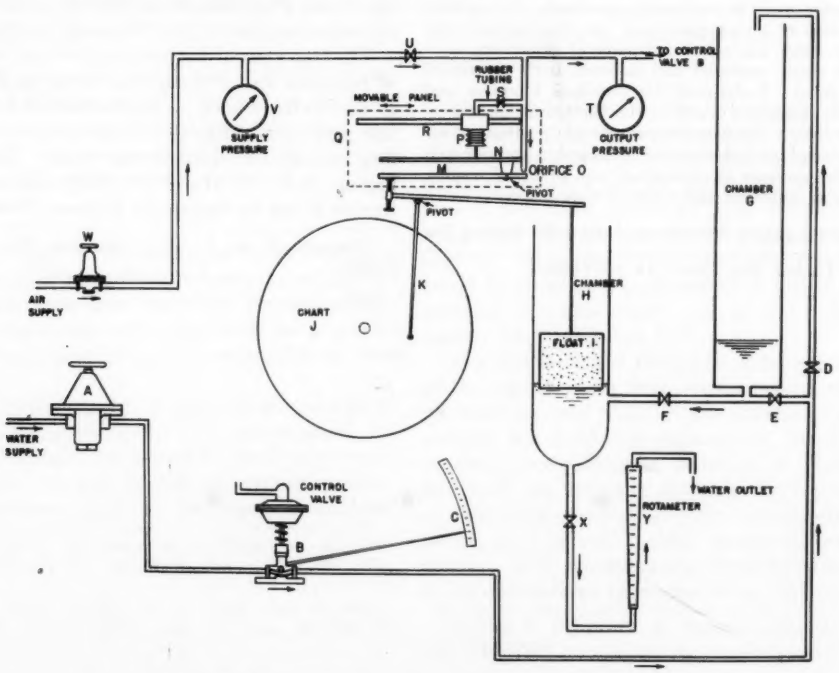


Figure 2. Schematic Diagram of Instrumentation Teaching Aid

shown in Figure 2. In this particular apparatus liquid level in chamber H is the controlled variable. The measuring element consists of a float I whose position is transmitted mechanically to the pen arm K and the air orifice O. Water enters chamber H through an air-operated control valve B. Chamber G is connected in series with H whenever the effect of process lag is to be studied.

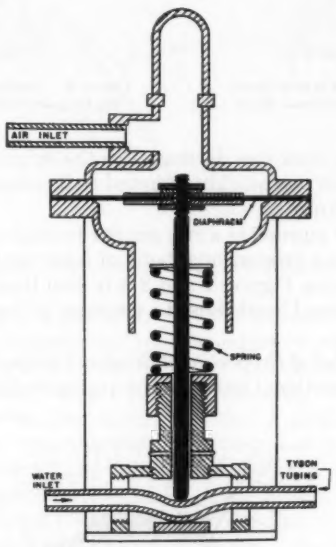


Figure 3. Control Valve

The position of the float determines the distance of the flapper from the orifice, which in turn determines the air pressure on the diaphragm of the control valve.

The proportional band is adjusted by either varying the effective length of lever arm M or by varying the effective length of lever arm N. The length of lever arm M is adjusted by sliding panel Q to the right or left. The length of lever arm N is adjusted by sliding the bellows P to the right or left along track R.

Water leaves chamber H through manually operated valve X, which controls the load on the system. The load is measured by means of rotameter Y.

The air-operated control valve B was constructed from an automobile fuel pump and a $^1/_4$-inch screwed brass globe valve. The construction of the control valve is shown in Figure 3.

The circular chart J makes one revolution per hour and is rotated counterclockwise by means of a motor taken from a dime-store variety alarm clock. The hub which holds the chart was soldered to the shaft that rotates the minute hand of the clock mechanism. In order to obtain a counterclockwise rotation of the chart, the clock mechanism was mounted with its reverse side facing the control panel.

With this apparatus it is possible to obtain simple on-off action, proportional action, and proportional with derivative action. Although it is not employed in this apparatus, automatic reset action may be incorporated by the addition of a second bellows and resistance combination.

TYPICAL EXPERIMENTS

Four typical experiments which may be conducted with the use of this teaching aid are described below.

(*1*) *Determination of Proportional Band.* The width of the proportional band is defined as the number of chart units over which the recording pen must travel in order to cause the control valve to move from the completely closed to the completely open position. The percentage proportional band is equal to 100 times the ratio of the width of the proportional band to the range of the instrument.

In order to determine the proportional band, the operator moves the pen-arm manually until the output pressure on gage T reads 15 psig. This represents the completely closed position of the control valve. The chart reading is noted. The pen-arm is then moved until the output pressure on gage T reads 3 psig, which represents the completely open position of the valve. The chart reading is again noted. Intermediate values of output pressure versus chart reading may also be obtained if desired.

Figure 4 shows the record which was obtained when the pen-arm was moved stepwise to produce two psi increments of pressure change on gage T. The data obtained were as follows:

Chart reading	*Output pressure, psig*
+9.6	15 (valve fully closed)
+6.6	13
+2.8	11
−1.2	9
−5.5	7
−9.6	5
−13.7	3 (valve fully open)

The width of the proportional band in the above case is equal to $9.6 - (-13.7) = 23.3$ units. The range of the instrument is 42 units. The percentage proportional band for this particular setting is therefore equal to $^{23.3}/_{42} \times 100 = 55.5$ per cent. Figure 5 shows a similar run, in which the proportional setting of the instrument was 12 per cent.

A plot of the data from Figures 4 and 5 is presented in Figure 6. It will be noted that output pressure is essentially a linear function of the chart reading.

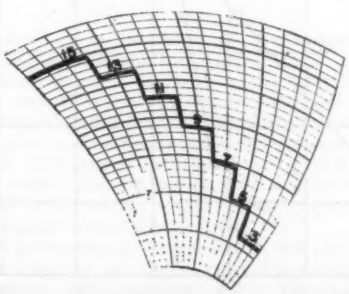


Figure 4. Liquid Level at Different Output Pressures. 55.5% Proportional Band

(2) *Effect of Process Load on Offset.* Offset is defined as the difference between the actual value of the controlled variable and the desired value or set-point. The object of the present experiment is to show that offset is produced by a change in process load and that offset decreases as the proportional band is decreased.

Figure 7 shows the results of a run in which the load was varied for a proportional setting of 30 per cent. The run was made without the use of chamber *G*, *i. e.*, with essentially no process lag. Referring to Figure 7, the load between points 1 and 2 was 100 cc./min. At point 2 the load was suddenly increased to 200 cc./min. It will be noted that the chart reading or liquid level in chamber *H* quickly dropped from a value of 8.0 to 7.8

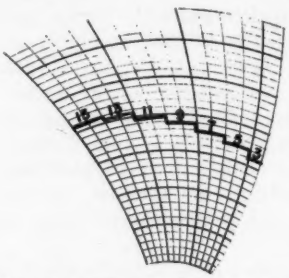


Figure 5. Liquid Level at Different Output Pressures. 12% Proportional Band

units. At point 3 the load was increased to 400 cc./min. with a corresponding drop in liquid level to 7.4 units. At point 4 the load was increased to 800 cc./min. with a corresponding drop in liquid level to 7.0 units. At

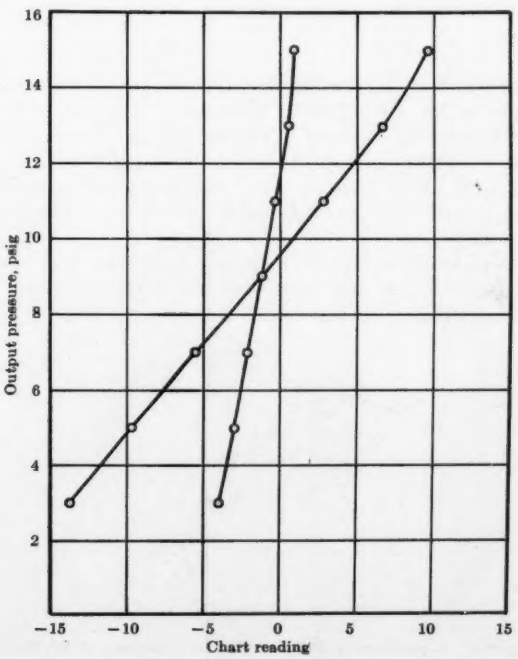


Figure 6

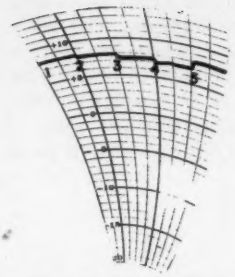


Figure 7. Varying Load. 30% Proportional Band

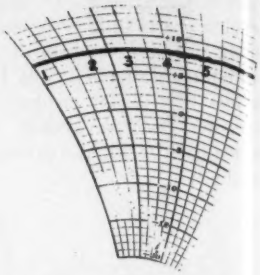


Figure 8. Varying Load. 5% Proportional Band

point 5 the load was decreased to the original 100 cc./min. and the pen quickly returned to its original control point of 8.0 units.

Figure 8 represents a run similar to that of Figure 7, except that a proportional band of 5 per cent was used. By comparing Figures 7 and 8 it is seen that a decrease in proportional band caused a decrease in the amount of offset.

(3) *Effect of Proportional Band on Cycling.* Too narrow a proportional band causes undue cycling for cases

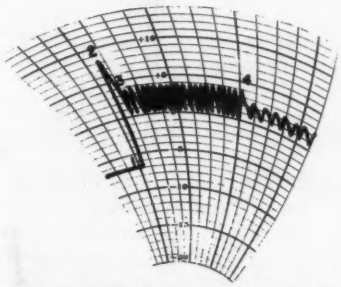


Figure 9. Process with Lag. 1.5% Proportional Band

where an appreciable process time lag exists. The present experiment shows how cycling may be eliminated by increasing the proportional band.

Figure 9 represents a run in which chamber *G* was introduced into the system to produce a process lag. A narrow proportional band of 1.5 per cent was employed. The chart shows the record of the liquid level in chamber *H*. At point 1 the water was turned on with a process load of 500 cc./min. The level quickly rose to a maxi-

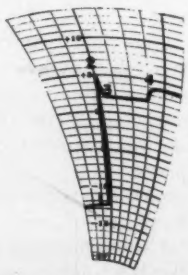


Figure 10. Process with Lag. 55% Proportional Band

mum at point 2 and then dropped to a steady cycling at point 3. At point 4 the load was suddenly lowered to 200 cc./min. The pen-arm continued to cycle but at a reduced amplitude and frequency.

Figure 10 represents conditions identical to those in Figure 9 except that the proportional band was in-

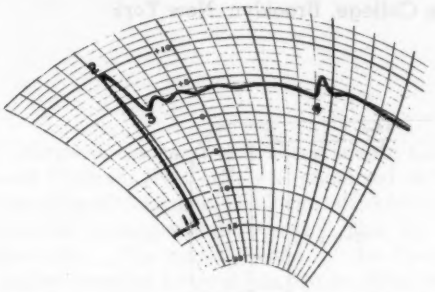


Figure 11. Process with Lag. 60% Proportional Band

creased to 55 per cent. It will be noted that the increased proportional band completely eliminated the cycling. It will also be noted that the larger proportional band caused less overshooting of the control point during the startup but that a greater offset was obtained when the load was changed at point 4.

Experiment 4. In some processes a wide proportional band is necessary in order to minimize cycling, but too great a length of time is required for the process to settle down after an upset. In these cases a controller with derivative action is desirable. Derivative action in the present apparatus is obtained simply by introducing a derivative resistance consisting of a laboratory screw-type pinchclamp shown as item *S* in Figure 2. The pinchclamp is adjusted manually by trial and error until the proper control is obtained.

Figure 11 shows the record of a run in which a proportional band of 60 per cent was used. This run was similar to that of Figure 10 except that a greater load and a greater process lag were employed. At point 1 the run was started with a load of 700 cc./min. The liquid level cycled but the amplitude of the cycle kept diminishing. At point 4 the load was suddenly lowered to 250 cc./min.

Figure 12 represents a run identical to that of Fig. 11 except that derivative action was employed. It is seen that derivative action very successfully reduced

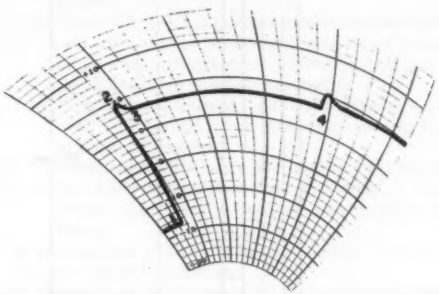


Figure 12. Process with Lag. Derivative Action. 60% Proportional Band

the time required for the process to reach equilibrium. It also very materially reduced the overshooting of the control point during the startup and following the load change.

SUMMER COURSE IN RADIOACTIVITY

THE Special Training Division of the Oak Ridge Institute of Nuclear Studies, Oak Ridge, Tennessee, has scheduled a two-week summer course on radioactivity, designed for teachers of science education and secondary-school science.

Entitled "Special Course in the Use of Radioisotopes in Secondary School Science Teaching," the course will begin on June 7, and will consist of background lectures in physics and radioactivity. Also included in the curriculum will be demonstrations of the experiments outlined in the recent Atomic Energy Commission booklet, "Laboratory Experiments with Radioisotopes," by Samuel Schenberg and John H. Harley. This booklet is based on a science education program developed by the Board of Education of the City of New York.

Emphasis throughout the course will be on the technique of using radioisotopes in classroom and laboratory.

Attendance will be limited to 60 participants, who will be selected from the following two groups: (1) those persons active in high-school science teaching or in the supervision of science teaching; and (2) representatives of college and university departments of education who are interested in introducing radioisotope techniques into their science education courses.

This is the first such course to be offered by the Special Training Division, which conducts regular basic courses in radioisotope techniques, and schedules certain special and advanced isotope courses designed to meet specific needs.

Further information about this course, and application blanks, may be obtained by writing the Special Training Division, Oak Ridge Institute of Nuclear Studies, Box 117, Oak Ridge, Tenn.

EFFICIENT ABSORPTION TRAP FOR NOXIOUS GASES

IRVING ALLAN KAYE, LOUIS SATTLER, and ROGER TWEED
Brooklyn College, Brooklyn, New York

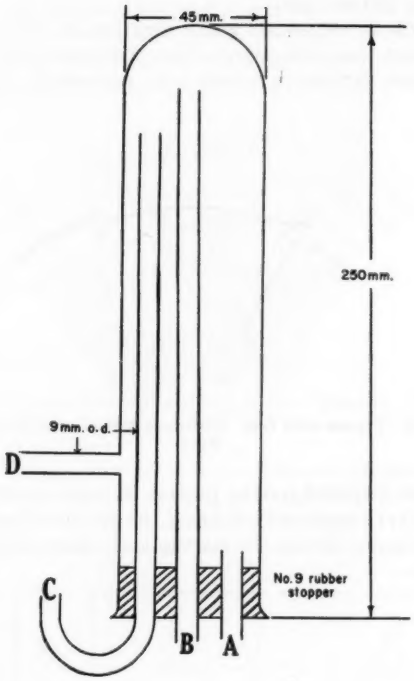


Figure 1

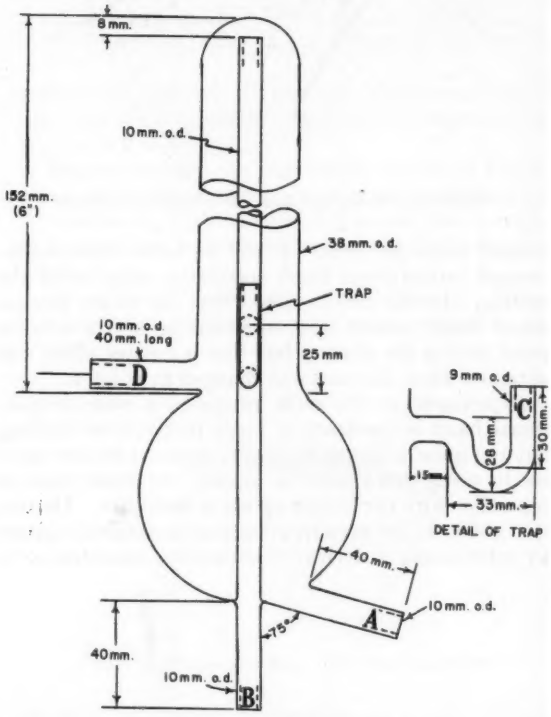


Figure 2

THE trap shown in Figure 1 is readily constructed from available laboratory materials, is efficient in taking care of rapid surges of gas, and has a safety feature which prevents the backing-up of water into the reaction vessel when the flow of water is interrupted.[1] Figure 2 is an all-glass version of the apparatus.

In use the exit waters from the condenser enter the trap at *A* and leave at *D*, thus forming a moving pool of water in which the water-soluble gases are trapped and at the same time creating a gentle vacuum. The noxious gas coming from the top of the condenser enters at *B*. The bend of *C*, sealed off with a drop or two of water, acts as a safety valve. The ends of *A* and *B*, outside the side-arm test tube, are best shaped, like *C*, in the form of U-bends.

When *A* and *C* are sealed off with pieces of rubber and Hofmann screw clamps, the apparatus may be used as a steam trap, the steam entering at *D* and leaving at *B*. The water, collecting at the bottom of the apparatus, is removed continuously through *A* by opening its clamp just wide enough to permit escape of the water.

[1] For other designs of gas traps see FIESER, L. F., "Experiments in Organic Chemistry," D. C. Heath and Co., New York, 1941, pp. 54, 313; and SATTLER, L., *Chemist Analyst*, **35**, 71 (1946).

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NATIONAL COOPERATIVE UNDERGRADUATE CHEMICAL RESEARCH PROGRAM

ETHALINE CORTELYOU
Armour Research Foundation, Chicago, Illinois
W. P. CORTELYOU
Roosevelt College, Chicago, Illinois

THE National Cooperative Undergraduate Chemical Research Program (NaCUR) was organized at the St. Louis meeting of the American Chemical Society in 1948 to stimulate undergraduate research and to supply chemical data. The major premise of the Program is that usable chemical information can be obtained from duplicating work done by two or more undergraduate students in different schools, independent of and unknown to each other.

Early in the five years of its active existence, it became obvious that an additional purpose served by the Program is to stimulate or revive research interest in teachers of small schools who previously have felt handicapped by limited funds, facilities, time, and research-quality students. We now have a project sponsored by an industrial chemist listed for the second year. So we may have added a fourth aim: to give industry an opportunity to participate in the stimulation of undergraduate chemical research to help insure for itself a continuing supply of young chemists and chemical engineers.

For the 1954–55 school year the National Cooperative Undergraduate Chemical Research Program offers 19 projects for student participation. The outline used for each project is:

(*a*) Typical unit assignment
(*b*) Special equipment needed
(*c*) Special chemicals needed
(*d*) Minimum student prerequisite
(*e*) Name and address of Director

ANALYTICAL PROJECTS

1. *Sensitivity of Inorganic Qualitative Analysis Reagents*
   (*a*) Determine the number of milligrams (in solution) of each of a group of cations required to give a characteristic reaction with 1.0 ml. of each of several different reagent solutions under specified conditions.
   (*b*) 24 small reagent bottles (30–100 ml.) with droppers in the stoppers, or any convenient means of counting the drops of solutions used.
   (*c*) Salts to prepare the cation solutions; sometimes special organic reagents.
   (*d*) Completion of a course in systematic qualitative analysis.
   (*e*) W. P. Cortelyou, Roosevelt College, Chicago 5, Illinois.
2. *The Magnitude of Some Simple Quantitative Technique Errors*
   (*a*) Is it necessary to grease the lid of a desiccator?
   (*b*) Usual instruments and equipment needed for volumetric and gravimetric quantitative analyses.
   (*d*) Quantitative analysis.
   (*e*) Ethaline Cortelyou, Department of Chemistry and Chemical Engineering, Armour Research Foundation of Illinois Institute of Technology, Chicago 16, Illinois.
3. *Use of Paper Chromatography in Qualitative Analysis*
   (*b*) Sheets and rolls of Whatman filter paper prepared for paper chromatography; wide-mouthed jars or bottles, 12 to 15 inches tall, are useful.
   (*c*) Salts to prepare cations; solvent solutions, *e. g.*, acetic acid, sulfuric acid, butanol, isopropanol, and other alcohols, if desired.
   (*d*) General chemistry and some qualitative analysis.
   (*e*) Sister Alice Marie, Associate Professor of Chemistry, Mount St. Mary's College, Los Angeles 49, California.
4. *The Development of Quantitative Volumetric Determination of Paint Pigment Constituents*
   (*a*) Comparison of five assigned internal indicators for the titration of zinc.
   (*c*) Special indicators assigned.
   (*d*) Quantitative analysis.
   (*e*) Clovis Adams, The Sherwin-Williams Company, 115th Street and Cottage Grove Avenue, Chicago, Illinois.

INORGANIC PROJECTS

5. *Solubilities of Inorganic Sulfamates in Water*
   (*a*) Determination of the solubility of barium sulfamate in water at 20°, 30°, 40°, and 50°; includes preparation and purification of the barium sulfamate.
   (*b*) Screw-cap bottles of approximately 125-ml. capacity; suitable shaking device for six or eight bottles in a thermostat.
   (*c*) Reagent grade sulfamic acid.
   (*d*) Good background in quantitative analysis.
   (*e*) Sister Agnes Ann, Immaculate Heart College, Los Angeles 27, California.
6. *Solubilities of Inorganic Fluoride Salts in Organic Solvents*
   (*a*) Determination of solubility of potassium fluoride in dioxane at several temperatures.
   (*b*) Constant temperature bath; containers not affected by compounds used, probably polyethylene bottles.
   (*c*) The inorganic fluoride and the organic solvent used.
   (*d*) Elementary quantitative analysis and elementary organic chemistry.
   (*e*) John H. Walkup, Centre College, Danville, Kentucky.
7. *Solubilities of Inorganic Halides (Other than Fluorides) in Organic Solvents*
   (*a*) Determination of solubility of lithium bromide in *n*-butyl alcohol at 0°, 25°, and 100°C.
   (*b*) Constant temperature bath; screw-cap, glass bottles of approximately 100–125 ml. capacity; shaking device.
   (*c*) None, other than good grade solute and solvent.
   (*d*) One quarter of quantitative analysis or at least be pursuing same.
   (*e*) Kirby E. Jackson, University of Alabama, University, Alabama.

ORGANIC PROJECTS

8. *Preparation and Characterization of Diamides from Methylene Bis-(4-phenyl isocyanate) and Alkyl or Aryl Bromides Through the Grignard Reaction*
   (*a*) Condensation of the RMgX compounds of three or four alkyl or aryl bromides with methylene *bis*-(4-phenyl isocyanate) and subsequent hydrolysis to the diamide, methylene *bis*-(*p*-acyl aniline); the purification of the diamides and determination of physical constants.
   (*b*) Two-neck, round-bottomed flasks.
   (*c*) Methylene *bis*-(4-phenyl isocyanate), alkyl or aryl bromides, metallic magnesium for Grignard reagents, dry ether.
   (*d*) Elementary organic chemistry.
   (*e*) Roy G. Bossert, Ohio Wesleyan University, Delaware, Ohio.
9. *Preparation and Properties of Acylacenaphthenes*
   (*a*) Preparation and properties of 5-(*p*-toluyl)-acenaphthene.
   (*b*) General organic laboratory equipment.
   (*c*) Acenaphthene, *p*-toluyl chloride, carbon disulfide, hydroxylamine hydrochloride, phenylhydrazine hydrochloride, etc.
   (*d*) Organic chemistry.
   (*e*) Edith J. H. Chu, Immaculate Heart College, Los Angeles 27, California.
10. *Characterization of Amines as Salts of Oxalic Acid*
   (*a*) Preparation and crystallization of desired salts and determination of melting points of these derivatives.
   (*b*) Good standard thermometer.
   (*c*) Primary amines.
   (*d*) Two semesters of organic chemistry and preferably a course in qualitative organic chemistry.
   (*e*) Sister Mary Daniel, C.C.V.I., Incarnate Word College, San Antonio 9, Texas.
11. *Preparation of Certain Schiff Bases and Their Reduction with Lithium Aluminum Hydride*
   (*a*) Synthesis of octadecylbenzylideneamine and reduction to N-octadecylbenzylamine.
   (*b*) Three-neck flask; mechanical stirrer; Claisen flask; and, for most preparations, a vacuum pump.
   (*c*) Lithium aluminum hydride.
   (*d*) Elementary organic chemistry.
   (*e*) Bertin L. Emling, St. Vincent College, Latrobe, Pennsylvania.
12. *Preparation and Characterization of Aromatic Compounds by the Friedel-Crafts Reaction*
   (*a*) Condensation of a cyclic anhydride with an aryl compound; purification and characterization of the product.
   (*b*) Stirring motor.
   (*c*) A series of hydrocarbons; anhydrous powdered aluminum chloride; tetrachloroethane or nitrobenzene.
   (*d*) Organic chemistry and quantitative analysis.
   (*e*) John D. Reinheimer, The College of Wooster, Wooster, Ohio.
13. *Determination of Missing Items of Data in the Tables of Physical Constants of Organic Compounds in Lange's Handbook, Especially Refractive Indexes and Boiling Points*
   (*b*) Refractometer, 0.1-°C. thermometers or better.
   (*d*) Organic chemistry.
   (*e*) Sarkis Kalfayan, Mount St. Mary's College, Los Angeles 49, California.

PHYSICAL PROJECTS

14. *Determination of Refractive Indexes of Binary Liquid Mixtures at Various Concentrations and Various Temperatures*
   (*a*) Determination of refractive indexes of dioxane-ethylene glycol solutions of various concentrations at some given temperature.
   (*b*) Good refractometer, constant temperature water bath, circulating pump.
   (*c*) The liquids to be used.
   (*d*) Elementary quantitative analysis and elementary organic chemistry.
   (*e*) R. I. Rush, Centre College, Danville, Kentucky.
15. *Binary Azeotropes to Members of Hydrocarbon Homologous Series with Glycol Ethers*
   (*a*) Study of the vapor-liquid equilibrium compositions as a function of boiling temperature for azeotropic agent with one or more pure hydrocarbon homologues.
   (*b*) Efficient fractionation column, Abbé refractometer; manostat desirable but not necessary.
   (*c*) Carefully purified liquids.
   (*d*) Physical chemistry taken concurrently.
   (*e*) William F. Kieffer, The College of Wooster, Wooster, Ohio.
16. *Determination of Ternary Azeotropes Containing Water and Amines and/or Alcohols*
   (*a*) Investigation of toluene, methyl cellosolve, and ethyl alcohol system.
   (*c*) Carefully purified liquids of the particular system studied.
   (*d*) Physical chemistry taken concurrently.
   (*e*) H. E. Weissler, Incarnate Word College, San Antonio, Texas.
17. *Determination of the Reliability of Ideal Laws in Typical Practical Circumstances*
   (*a*) Determination of the molecular weight of naphthalene from its freezing-point depression in benzene at several concentrations to observe departure from ideality as a function of concentration
   (*d*) Physical chemistry.
   (*e*) Nathan Yagol, Roosevelt College, Chicago 5, Illinois.
18. *Chemical Means of Cleaning Ultramicro Pipets*
   (*e*) George F. Hand, State Microscopical Society of Illinois, 7512 Olcott Avenue, Hammond, Indiana.

BIOCHEMICAL PROJECT

19. *Determination of Amino Acids by Paper Chromatography*
   (*b*) Whatman No. 1 filter paper.
   (*c*) Individual amino acids, ninhydrin.
   (*d*) 24 hours of chemistry.
   (*e*) Sister Mary Daniel, C.C.V.I., Incarnate Word College, San Antonio 9, Texas.

Each of the projects listed is considered simple and objective enough for stimulating undergraduate work. A project is divided into research units, each of such a nature that acceptable results and a report can be achieved in 50 laboratory hours, the usual requirement for one semester-hour college credit.

Any teacher who has one or more students interested in a particular project is invited to write directly to the Project Director. The Project Director will furnish an individual assignment for each student. The student's own teacher will direct him in the laboratory work required by the assignment and in the preparation of an acceptable research report for submission to the Project Director.

A Certificate of Acceptance will be awarded to each student submitting a report accepted by a Project Director. The certificates are signed by the student's own teacher, by the Project Director, and by the president and secretary of Handbook Publishers, Inc., who have generously provided the printed certificate form. Suitable data may be selected for publication in the

'Handbook of Chemistry." A Project Director may publish data obtained on several units as a paper giving full credit to participating students and schools.

One NaCUR project has been completed and the results reported in a paper read at the Buffalo, 1952, A. C. S. Meeting.[1] Several students have reported their results in papers before student affiliate groups of the A. C. S. and state academies of science.

[1] EMLING, BERTIN, "Some alkyl benzenesulfonates," *J. Am. Chem. Soc.*, **74**, 4702–4 (1952).

Any teacher or industrial chemist interested in directing a new project should write to one of the authors as soon as possible, since a project is listed under the direction of the first person to request it. An outline of any project for the 1955–56 school term must be sent in by January 10, 1955.

NOTE: Since this went to press, the following project was added: *Organic Project: Synthesis of Polynuclear Compounds*, E. G. Bordwell, Northwestern University, Evanston, Illinois.

Proceedings of the

PACIFIC SOUTHWEST ASSOCIATION OF CHEMISTRY TEACHERS

COMBINED MEETING AT SAN LUIS OBISPO

THE Pacific Southwest Association of Chemistry Teachers met at the California State Polytechnic College at San Luis Obispo on January 8 and 9 to share ideas about the building of new laboratories.

More than fifty members heard Professor G. Ross Robertson discuss fundamental problems in chemistry building design. This address was an extension of material already published in THIS JOURNAL.[1]

A six-man panel on Saturday morning told of some of the unusual problems faced in the construction of new buildings. Naylor, at San Jose, described the special precautions needed when a three-story chemistry building is put up some twenty feet from the busiest intersection in the city. According to Draper, the buildings at Sacramento must somehow take care of present needs and yet leave room for great expansion. Benedict at Chico uses a punch-card system for taking care of breakages, and Mooney reported that because no reader help can be supplied at El Camino, class enrollments are kept below thirty. Cooperation is a necessity at Santa Barbara, where, according to Bickerdike, geology, chemistry, physics, and all of the biological sciences share the same building.

Although Morse of San Francisco stressed the lack of information concerning the design and building of science facilities, the meeting produced a number of valuable suggestions, and anyone contemplating the construction of new facilities would do well to write to members of this experienced panel for answers to specific questions.

After some discussion of the panel presentation, there was still a little time to hear Dr. Frank Lambert's description of his molecular models made from Styrofoam.[2]

After lunch and a short business meeting which included the installation of new officers, members of the Chemistry Department at Cal Poly provided buses for a tour of the local campus. On this tour, the visiting professors were given an enthusiastic description of the excellent building program planned for this unusual college.

This combined meeting was generally considered most successful. Although the local faculty made careful plans for a good part of the time, there was ample opportunity for informal discussion in small groups. San Luis Obispo is ideally located, not too far from the heavily populated south, nor beyond the reach of people from Chico and Humboldt in the north. There seems to be considerable sentiment in favor of making the combined meeting at this institution an annual affair.

[1] ROBERTSON, G. ROSS, "Chemistry at UCLA," J. CHEM. EDUC., **30**, 526–8 (1953).

[2] LAMBERT, FRANK L., "Molecular models for lecture demonstrations in organic chemistry," J. CHEM. EDUC., **30**, 503–7 (1953).

Report of the

NEW ENGLAND ASSOCIATION OF CHEMISTRY TEACHERS

RATES OF SUBSTITUTION REACTIONS IN OXYANIONS

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In the chemistry of the oxyanions, little is known about the factors which influence rates of replacement reactions such as:

$$SO_3Cl^- + OOH^- \rightleftharpoons SO_3OOH^- + Cl^-$$

The rates are markedly dependent on the acidity of the media (*1*, *2*, *3*); this factor and other factors affecting the rates for the more common oxyanions are enumerated and discussed in the present article.

The oxyanion reactions to be considered are of the type:

$$SO_3X^- + Y^- \rightleftharpoons SO_3Y^- + X^-$$

where one group (Y^-) replaces another (X^-) with no obvious change in oxidation state of the oxyanion or of either of the substituent groups. As rates of replacement reactions involving sulfates have been studied often, the reactions of substituted sulfates will be used as examples wherever possible.

In the discussions concerning different oxyanions, use will be made of isotope exchange data if such data are available. It should be pointed out, however, that not all of the exchange studies are in agreement on the rates for some oxyanions. Further studies of oxygen-isotope exchange reactions, particularly of those oxyanions which appear to exchange rapidly, are certainly desirable. Other data where the substituent group is F^-, NHR^-, OOH^-, OR^- or any other electronically similar group have been used along with the exchange data. Hydrolyses of substituted oxyanions give particularly useful information. In some cases, rates of oxidation-reduction reactions will be employed, but only to augment other incomplete data. Taube (*2*), in his review on rates of replacements in inorganic complexes, gives an excellent discussion of substitution reactions and the criteria necessary for accurate judgment of their rates.

The importance of the acidity of the medium will be discussed first. The basicity of the group which is replacing (Y^-) will then be covered; this will be followed by a discussion of the effect of basicity of the departing group (X^-). Consideration of the factors such as the charge of the central atom that influence the rates of replacement reactions for particular oxyanions will then be given. Possible correlations of replacement rates with oxyacid acidities and with electronic structures will also be discussed.

While the conclusions drawn from the reactions of substituted sulfates and from the other examples are probably valid for most of the oxyanions, it should be emphasized that the natures of oxyanions are variable and that exceptions to almost any generalization can be found. This will be especially noticeable when more than one group different from O^{--} or OH^- is substituted on the oxyanion; for this reason, the present discussion is limited to mono-substituted oxyanions.

The Acidity of the Media. It has been postulated (*3*) that the often observed second-order dependence on hydrogen-ion concentration in the rate laws of oxyanion reactions with bases is related to the change in basicity of an oxide ion as hydrogen ions are added to form successively hydroxyl ion and water. Whether this is the correct explanation or not, it is certainly a fact that the hydrogen-ion concentration is a factor of utmost importance in the rates of oxyanion replacement reactions (*1*, *2*, *3*).

In reactions involving sulfates there are many examples which demonstrate the increase in rate as the acidity of the solution increases. Recently the rate law for exchange of oxygen atoms between SO_4^{--} and H_2O was investigated by Hoering and Kennedy (*4*). The rate of this exchange is proportional to the concentrations of HSO_4^- and H^+. Similar rate laws were found for the exchange of oxygen atoms between carbonates and water (*5*), and between organic carboxylate ions and water (*6*). Catalysis by acids and

inhibition by bases are found for most of those oxygen-isotope exchange reactions of oxyanions that have been studied (*7–11*).

The hydrolyses of substituted sulfates are catalyzed by acids. Some examples are the hydrolyses of amine sulfonates and hydroxylamine sulfonates (*12*), of peroxy-substituted sulfates (*13*), of alkyl sulfate ions (*14*), of aryl sulfate ions (*15*), and of dithionate ion (*16*). Hydrolysis reactions of substituted sulfates are further discussed in the section dealing with the basicity of the group that is being replaced.

The rates of formation of compounds such as benzene sulfonic acids (*17*), alkyl hydrogen sulfates (*18*), and peroxysulfates (*13, 19*) are strongly dependent on the acidity of the media.

Rate data on oxidation-reduction reactions are only useful in studies of replacement reactions in a few special cases, since the rate-determining step is often a collision step or an electron-transfer step. However, these rates are interesting, for the same dependence on hydrogen-ion concentration is found in reduction reactions of oxyanions by bases as is found in replacement reactions. The rate laws for these oxidations are in agreement with a mechanism in which the reducing agent (base) first replaces a water molecule in the oxyanion and in which the electron transfer occurs after a bond between the reducing agent and the central atom of the oxyanion has been formed (*3*).

In many of these oxidation reactions the replacement step may be the rate-determining step, for replacement reactions in certain oxyanions have high energies of activation. In cases where the replacement step is not rate-determining, it must be at least as fast as the rate-determining step. For example, H_2SeO_3 oxidizes I^- to I_2 (*20*) and $S_2O_3^{--}$ to $S_4O_6^{--}$ (*21*) in dilute acid solution, while H_2SeO_4, which is a stronger oxidizing agent, does not oxidize either I^- or $S_2O_3^{--}$ unless the solution is strongly acidic. It is probable that the rate-determining step in H_2SeO_4 oxidations is the replacement of an oxide ion (as H_2O) by the reducing base and that the electron transfer is a rapid follow-up step. One can conclude from these arguments that replacement reactions of selenate ion are slow. The two kinetic studies (*20, 21*) of selenious acid oxidations indicate that the rate-determining steps probably occur after rapid replacement steps; thus one can conclude that substitution in selenites is a fast process. These conclusions from rates of oxidation-reduction reactions are in good agreement with conclusions from isotope exchange studies (*7*).

Studies of the reactions of oxyanions in nonaqueous solvents give further evidence for the reactivity of the oxyanions as a function of the acidity of the media. Solutions of HNO_3 and H_2SO_4 in liquid ammonia show little or no oxidizing power; alkali metal permanganates and chromates are soluble in liquid ammonia but are weak oxidizing agents (*22*). This nonreactivity of the oxyanions can be traced at least in part to the fact that liquid ammonia is a more basic solvent than water. In the acidic solvent anhydrous liquid hydrogen fluoride oxyanions such as NO_3^-, SO_4^{--}, ClO_3^-, BrO_3^-, MnO_4^-, and CrO_4^{--} undergo drastic changes. Many of these changes are replacement reactions such as:

$$SO_4^{--} + 3HF \rightleftharpoons SO_3F^- + H_3O^+ + 2F^-$$

while others are decompositions (*23, 24*).

Although the acidity of the media plays an extremely important role in sulfate substitutions and in substitutions for almost all of the oxyanions, certain exceptions may be found. Substitution in periodate ion, for example, could take place readily without pH dependence in view of the known hydration reaction:

$$IO_4^- + 2H_2O \rightleftharpoons H_4IO_6^-$$

which is not slow to reach equilibrium (*25*). Base-catalyzed substitutions are also possible, although they are not generally important. Presumably this fact stems in part from the difficulty in removing a hydroxide ion or an oxide ion as compared to removing a water molecule.

The Basicity of the Group Y^-. Two different mechanisms for replacement in oxyanions fit the observed rate laws. The first, again using sulfates as examples, is a displacement reaction on sulfur,

$$HY + OSXH \rightleftharpoons HYSO + HX \qquad (1)$$

of the Walden Inversion type.[1] The second mechanism, which involves dissociation prior to replacement, is:

$$\left.\begin{array}{l} OSX^- + H^+ \xrightarrow{k_1} SO_3 + HX \\ SO_3 + HY \xrightarrow{k_2} SO_3Y^- + H^+ \end{array}\right\} \qquad (2)$$

In mechanism (1) the rate of replacement should increase as the basicity of Y^- increases. For mechanism (2) the basicity of Y^- probably should not affect the over-all rate of replacement but it should affect the product composition. The amount of data at hand is very small and does not enable a distinction to be made between these two possible mechanisms except for carbonates. Also, there are few data on the effect of the incoming group on the rates of the replacement reactions.

In weakly acid solutions HNO_2 appears to react more rapidly with hydroxylamine (to form hyponitrous acid and eventually N_2O) than with H_2O (to give oxide ion exchange (*27*)). These data are consistent with either mechanism.

[1] In highly conducting hydroxylic solvents such as H_2O it is somewhat arbitrary where the hydrogen ions are placed (*cf.* references *14a* and *26*). They are placed as shown above, since, for example, it should be easier to displace H_2O from SO_3 than OH^- from HSO_3^+.

TABLE 1
Basicity and the Rates of Reaction of Amines with CO_2

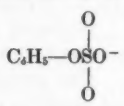
Amine	pK_b (18°)	k_2[a]	*Reference*
$C_6H_5NH_2$	~9.3	1.9×10^2	*32*
NH_3	4.76	3.8×10^4	*31*
$C_6H_5CH_2NH_2$	4.74	11.5×10^4	*32*
$CH_2{=}CHCH_2NH_2$	4.38	11.5×10^4	*33*
$H_2NCH_2CO_2^-$	4.24	6.7×10^4	*32*
CH_3NH_2	3.38	8.3×10^4	*31*
$(CH_3)_2NH$	3.22	6.7×10^5	*31*
$C_5H_{10}NH$	2.95	7.8×10^5	*32*

[a] Time in minutes, 18°.

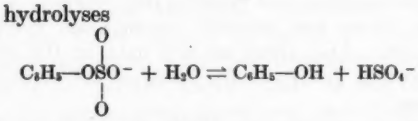
The mechanism of replacements in substituted carbonates has been investigated often; the most probable mechanism is (2), with k_2 being the rate-determining step (*5*). It is possible to study k_2 (the reaction of CO_2 with bases) under conditions where a suitable separation from the k_1 step is feasible. It was found (*5*, *28*) that OH^- reacts with CO_2 much faster than does H_2O; at 18° the bimolecular rate constant with OH^- is $\sim 1 \times 10^5$ (time in minutes) and the constant with H_2O (assuming $[H_2O]$ is 55 *M*) is $\sim 1.2 \times 10^{-2}$.

The rates of reactions of amines with CO_2 also depend on the basicity. In Table 1 data for rates and pK_b values are presented. There is no doubt that the rate of reaction of CO_2 with amines increases as the basicity of the particle increases. There are, however, large deviations from linearity in a plot of log k_2 against pK_b. This fact indicates that other factors, two of which may be the nucleophilic character of the base (*29*, *30*) and steric hindrance, are also influencing the reactions of bases with carbon dioxide.

The Basicity of the Substituent X^-. It might be expected that the rate of displacement of a group from an oxyanion would depend to some extent on the basicity of the substituent group. Evidence that basicity does play a role comes from careful investigations of the rates of hydrolyses of aryl sulfate ions (*15*). The aryl sulfates are ions of the type:



Their hydrolyses



proceed according to the rate law:[2]

$$\frac{d[HSO_4^-]}{dt} = k[C_6H_5OSO_3^-][H^+]$$

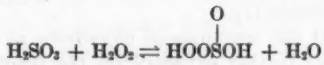
and the hydrolyses probably take place by breaking of the sulfur-oxygen rather than the carbon-oxygen bond (*15*).

Groups substituted on the meta and para positions of the benzene ring of the aryl sulfate ion cause significant differences in the rates of the hydrolyses of aryl sulfate ions. The rates of the hydrolyses of these substituted aryl sulfate ions, the pK_a values for most of the correspondingly substituted phenols (in 30 per cent ethanol) (*34*), and the sigma values of Hammett (*35*) for each of the substituent groups are presented in Table 2. The data indicate conclusively that the rates of the hydrolyses of aryl sulfate ions are related to the basicities of the corresponding phenolate ions. The rho value for phenol ionization in H_2O is +2.008 while that for the hydrolyses is +0.467.[3] It can be concluded that the electron availability plays a lesser, though still significant, role in the hydrolyses of aryl sulfate ions than it does in the ionization equilibria of phenols. As expected, the hydrolysis rate decreases as the basicity of the group increases.

The data just presented show conclusively that the basicity of the group being displaced has an effect on the rate. This conclusion does not warrant extrapolation to cases where the groups being displaced are not closely similar. For example, the strengths of the acids $HS_2O_3^-$, HSO_4^-, and HF decrease in that order (although the differences are small), yet the hydrolysis of $S_2O_7^{--}$ is very rapid (*36*) and the hydrolyses of $S_3O_6^{--}$ (*37*) and SO_3F^- (*38*) are quite slow. These data, plus other data of similar type, indicate that factors other than basicity influence the rates of hydrolysis of substituted oxyanions.

The Oxidation State of the Central Atom. In cases of elements which form several oxyanions in more than one oxidation state it is usually found that the rates of replacement reactions for the lower oxidation state are faster than those for the higher oxidation state.

The rates of reactions of the two sulfur oxyanions are excellent examples. As has been mentioned, the rates of replacement in substituted sulfates are almost always slow. Replacements in substituted sulfites are, on the other hand, almost invariably too fast to measure. Oxygen-isotope exchange of sulfite ion with water seems to be rapid even in alkaline solution (*8*). Many oxidations of sulfites appear to take place through replacement reactions on sulfur and some of these reactions are immeasurably rapid (*8*). A particularly interesting case is the oxidation of sulfite in acid solution by hydrogen peroxide. Both oxygen atoms of isotopically labeled peroxide end up in the product sulfate (*39*). This rapid reaction probably proceeds through peroxysulfurous acid, formed by the replacement (on sulfur) reaction,



as an intermediate.

The rate results with selenium, the next higher congener of sulfur, are similar. Some of the evidence for rapid replacement in selenites and slow replacement in selenates was discussed in a previous section.

Another oxyanion pair of this type is found in the

[2] Brackets are employed to denote concentration.

[3] The reported value of rho in Hammet (*35*) is −0.467 which probably is a typographical error in the sign.

chemistry of nitrogen. Although conclusive data are not available, it appears to be generally true that reactions of NO_2^- are considerably faster than reactions of NO_3^- and that many of the reactions of these oxyanions have one step which involves the formation of a new bond on the nitrogen atom (*1*, *27*, *40*). The nitrite reactions proceed in dilute acid solutions at room temperature, whereas reactions of nitrate ion generally need strong acid and high temperatures to proceed.

A final series concerns the element chlorine in its four positive valence states that occur as oxyanions. Again the data are not conclusive, but the order of decreasing replacement rate seems to be:

$$ClO^- > ClO_2^- > ClO_3^- > ClO_4^-$$

There is no doubt that perchlorate reactions are extremely slow, that hypochlorite reactions are rapid, and that the other two anions have intermediate rates.

Charge on the Central Atom. Although this factor is undoubtedly linked closely to the previous one, it was decided to keep them separate, as the situation is not completely clear. In a particular period of the periodic chart it seems to be a good generalization that the rates of replacement reactions decrease as the charge increases on going from left to right.

Consider the ions $H_2SiO_4^{--}$, HPO_4^{--}, SO_4^{--}, and ClO_4^-. Silicate ion seems to exchange its oxide ions rapidly with H_2O (*10*) and the other replacement reactions of silicates also appear to be fast. Phosphate reactions are generally slow, but seem to be faster than sulfate replacements. It is interesting to note that no careful study concerning replacement rates has ever been made on any perchlorate reaction; there is no question, however, but that perchlorate substitutions must be exceedingly slow.

Similarly, it has been found that borates undergo replacement reactions immeasurably rapidly (*30*), carbonates react rapidly in acid solution but slowly in base (*5*, *31–33*), and nitrates react extremely slowly in all but strong acid (*41*).

Sulfites react more readily than do either chlorates or chlorites (*8*). Selenites replace more readily than bromates (*7*).

There does seem to be some evidence that diprotic acids whose coordination number is less than their usual maximum will exchange at a rapid rate in acidities where monoprotic acids (of comparable structure or acid strength) do not. An explanation for this may be found in the reactions:

$$HAO_m + H^+ \rightleftharpoons AO_{m-1}^+ + H_2O$$

and

$$H_2AO_m \rightleftharpoons AO_{m-1} + H_2O$$

In order to lose a water molecule from a monoprotic acid (or to have H_2O displaced by another particle) it is necessary that an additional proton be present in the transition state. In order to lose a water molecule from a diprotic acid, no protons need be added since the acid has two protons already present.

The relative slowness of tetrahedrally substituted oxyanions as compared to the nontetrahedrally substituted oxyanions suggests that the mechanism of replacement is a nucleophilic attack by the incoming group. Consider the series $HClO_2$, H_2SO_3, and H_3PO_4. These acids are similar in strength; $HClO_2$ exchanges oxide ions slowly (*8*) as does H_3PO_4 (*11*), while H_2SO_3 and even sulfites appear to exchange extremely rapidly (*8*). The slowness of the $HClO_2$ exchange seems reasonable when explained on the basis of the need for an additional proton before replacement of a water molecule. The slowness of the H_3PO_4 exchange seems reasonable when explained on the basis of the oxygen tetrahedra around the phosphorus, acting as a shield to prevent the nucleophilic attack by a water molecule. The rapidity of reactions involving sulfites is reasonable since neither of the above two explanations should be true for SO_3^{--}, which has a pyramid structure with sulfur at the apex (*42*).

Other data indicate that the carbonate ion exchange (*5*) is faster than the nitrite ion exchange (*27*), although it is not definite.

The Size of the Central Atom. In any family of the periodic table there seems to be an increase in rates of oxyanion replacement reactions as the atomic number becomes larger. Probably the best example for this is found in the rates of reactions involving chlorates, bromates, and iodates.

Iodate ion was observed to exchange its oxide ions with H_2O rapidly in neutral solution, whereas bromate and chlorate exchanged slowly (*8*). This difference has been attributed by Halperin and Taube (*8*) to the tendency of pentavalent iodine to assume coordination numbers larger than three. Other exchange studies (*7*) have indicated that BrO_3^- exchanges more readily than ClO_3^-. The exchange studies agree well with rates of oxidation reactions of the halates; IO_3^- reacts more rapidly than BrO_3^-, which reacts more rapidly than ClO_3^-.

It has been found that arsenates exchange much more rapidly than do phosphates (*7*). It is also known that periodate undergoes replacement reactions rapidly,

TABLE 2

Effect of Substituents on the Benzene Ring on the Basicity of Phenols and on the Hydrolysis Rates of Aryl Sulfate Ions

Substituent	σ[a]	pK_a (C_6H_5OH)[b]	$k(\times 10^5)$ 48.6°[c]
p-NO_2	+1.27	7.69	44.5
m-NO_2	+0.710	9.02	20.5
m-Cl	+0.373	9.89	16.3
p-Br	+0.232	10.15	11.5
p-Cl	+0.227	10.20	10.8
m-OCH_3	+0.115	10.67	10.2
H	0.000	10.85	8.9
m-CH_3	−0.069	10.98	8.8
p-CH_3	−0.170	11.14	6.87
p-OCH_3	−0.268	...	4.50

[a] Ref. *35*.
[b] In 30% aqueous ethanol at 25°; data from ref. *34*.
[c] Units of *k* are liters per mole per second; a similar set of data were obtained at 78.7°; data from ref. *15*.

TABLE 3
Replacement Rates and Acidities of Oxyacids

Oxyacid	*pK_a*	*Rate conclusions*	*References*
$HClO_4$	(∼−8?)	Exceedingly slow	*7, 43*
$HMnO_4$	(∼−7?)	Measurable in acid solution	*7, 39*
H_2SO_4	(∼−3?)	Measurable in strong acid solution	*4, 15*
H_2SeO_4	(∼−3?)	Measurable in strong acid solution	*7, 44*
H_2CrO_4	∼0	Measurable in alkaline solution	*11, 45*
H_2MoO_4	(∼0?)	Rapid	*7, 46*
H_2WO_4	(∼0?)	Rapid	*7, 46*
$HClO_3$	(∼−1?)	Measurable in ∼1 *N* acid solution	*7, 8, 47*
$HBrO_3$	(∼0?)	Measurable in weak acid solution	*7, 8, 47*
HIO_3	0.7	Rapid in neutral solution	*7, 8, 47*
HNO_3	∼−1	Measurable in strong acid solution	*41, 48*
H_5IO_6	1.6	Rapid in neutral solution	*25, 49*
H_3PO_4	2.1	Measurable in acid solution	*11, 50*
H_3AsO_4	2.3	Rapid	*7, 51*
H_2CO_3	3.4	Measurable in alkaline solution	*5, 31–33*
H_2SO_3	1.8	Rapid	*3, 7, 39*
H_2SeO_3	2.5	Rapid	*7, 20, 21*
HNO_2	3.4	Measurable in weak acid solution	*3, 27, 40*
$HClO_2$	1.9	Measurable in acid solution	*8, 52*
H_4SiO_4	∼10	Rapid	*10, 53*
H_3BO_3	9.2	Rapid	*10, 30*
H_3AsO_3	9.2	Rapid	*7, 54*
HClO	7.4	Measurable in alkaline solution	*55, 56*
HBrO	8.7	Rapid	
HIO	∼11	Rapid	

while perchlorate probably reacts more slowly than any other known oxyanion.

The increase in rate as the atomic number increases is, no doubt, connected with the larger size of the central atom. The larger size of the central atom aids in the formation of a transition state with a coordination number one greater than the usual coordination number.

Replacement Rates of Individual Oxyanions. In Table 3 qualitative conclusions concerning the rates of replacement reactions of 25 oxyacids are presented, along with pK_a values for the acids and some references pertinent to the conclusions on the rates. The word "slow" indicates that the rate of attainment of equilibrium conditions takes days or longer; the word "measurable" means that the rate constant can be measured by normal kinetic procedures; the word "rapid" means that the state of equilibrium is reached in a matter of seconds or less. Conditions are room temperature in aqueous solution.

Concerning H_6TeO_6 ($pK_a \simeq 9$) and H_2TeO_3 (pK_a = 2.7), there seem to be no data available upon which a direct conclusion on replacement rates can be based, although indirect evidence exists that indicates that replacement reactions for these oxyacids should be rapid.

Although no references are given for HBrO and HIO, the replacements on halogen for these molecules should be rapid since reactions of the type

$$HBrO + Br^- + H^+ \rightleftharpoons Br_2 + H_2O$$

are rapid.

One oxyacid, $HReO_4$, was not entered in the table as no data have been found allowing any judgment as to replacement rates. Presumably, the rates for $HReO_4$ should be faster than those for $HMnO_4$.

There is one important conclusion that should be pointed out. For any one oxyanion the rates of replacement are not markedly affected by the nature of group being displaced. For example, of all the substituted sulfates known, only two, $S_2O_7^{--}$ and SO_3Cl^-, appear to have rates of hydrolysis that are immeasurably rapid (and these may be slow in alkaline solution).

In substituted borates there are no known reaction rates that are measurable or slow.

Correlation of Rates with Acidities. Dr. A. D. Awtrey of Iowa State College suggested that a correlation could probably be found between the rates of replacement reactions of an oxyacid and the ionization constant of the oxyacid. In general it is noted in the data of Table 3 that acids whose pK_a is less than zero replace slowly or at a measurable rate and that acids whose pK_a is greater than seven replace rapidly. The correlation is no better than qualitative, though; this is to be expected, in view of the many factors influencing the rates of replacement reactions.

Correlation of Rates with Electronic Configurations. In his review on rates of replacement reactions in coordination compounds Taube (*2*) showed that the electronic structures of octahedral complexes with hybridized d^2sp^3 orbitals predominantly determined the rates of replacement reactions. The electronic structures of oxyacids certainly do not affect their rates of replacement reactions to any comparable degree, as is well demonstrated by the slow rates involving ClO_3^- and the exceedingly rapid rates involving the isoelectronic SO_3^{--}.

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To the Editor:

In his article, "Religious perspectives of college training" (J. CHEM. EDUC., **30**, 150 (1953)), drawing attention to the necessity for convincing technical students of the value of ethics, philosophy, and religion, Dr. Hugh S. Taylor fails to show the simple, logical connection between science and the humanities. The essence of his article can be found in his own remark: "The urgent need is not for the science specialist but for the liberally educated man," and "when man's capacity for control over the material through science is becoming ever more potent, it is even more essential that he pursue with equal intensity the principles of a spiritual order."

The response of many science specialists will be like this: "What is meant by the terms 'material' and 'spiritual'?" and "Why should specialists be liberally educated when the humanities will merely divert valuable effort from a more useful task?"

Dr. Taylor then completes his argument with: "Somehow or other the teacher of science must communicate in his teaching, in his work, in his life, the truth that our physical universe can go down into physical death unless we can at the same time make of it a sacramental universe." Now for those with a religious faith the idiom of the quotations is self-evident, but for those without, it is meaningless. My comment on Dr. Taylor's article is directed at those who have no faith and who consider ethics and philosophy as games. Let us consider more closely the opening remark of the article in question, which is as follows: "In the pursuit

of wisdom the teacher of science must find the opportunity to convince the student that beyond the areas covered by science and scientific conclusions, beyond the testimony of history, there are areas of truth which supplement those of knowledge to yield *sapientia.*" Now the central point of my argument is that the word "truth" has been used to cover two entirely different concepts associated with two clearly defined modes of thought. These modes of thought are, on the one hand, the rational, logical, and empirical; on the other, the moral, emotional, and the imaginative.

Let us consider the rational mode of thought. Our everyday experience compels us to conclude that the world around us behaves independently of our wishes; it has its own laws to which we must conform if we are to survive and if we are to control it in our limited way in order to satisfy our wishes. Rational thought is basically the cognition of the apparent order of our environment. Futile attempts to cope with a situation when the relevant data are known would then be defined as irrational behavior. Scientific work is a conscious effort at rational behavior and in the quest for scientific truth a constant reference is made to observed phenomena.

But the truth of a moral or artistic value cannot be determined empirically; it is what is known as a matter of opinion. The mental process underlying the spheres of morals and art has been called value-judgment. Statements approving or disapproving of any situation whatever comprise the process of value-judgment. Dr. Taylor has extended the term "truth" to cover statements of value.

Contrary to a widely held opinion, value-judgment is more fundamental to man than rationality. In all human activity there is a continuously operating process of valuation, conscious or subconscious, explicit or implicit. The whole of the vast accumulation of technical knowledge rests on a substratum of values no matter how heterogeneous. Rational thought is merely the tool whereby we fulfill our wishes: our wishes are an expression of what we have decided to call good or bad, and perhaps right or wrong.

Nevertheless, value-judgment and rationality interact; that is, as further knowledge is gained through rational procedures, value-judgments may change. Furthermore, once having accepted rational thinking as a mode of thought, no argument against the universal use of this tool has meaning. We are then compelled to investigate ethics in the light of rationality. In fact, we are merely compelled to investigate ethics, for even the most ascetic, secluded, rational, specialized scientist has made a value-judgment of the nature of "Science forever."

For men to attain the universal hope of universal happiness, they must be at least mutually aware of their values and attempt to agree and to act by rational thought.

BRUCE MCQUADE

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● ORGANIC CHEMISTRY

Harold J. Lucas, **Professor of Organic Chemistry, The California Institute of Technology. Second edition. American Book Company, New York, 1953. vi + 760 pp. 40 figs. 110 tables. 16.5 × 24 cm. $7.**

THIS is a revision of the well known textbook, the first edition of which was published in 1935. In the intervening eighteen years the field of organic chemistry has undergone considerable change and, needless to say, so has this excellent text; indeed, it is a tribute to the author that much of the material retained from the earlier edition required but little rewriting to bring it up to date.

The following is a statement from the preface: "One purpose of this edition is to meet the problems connected with an ever-expanding field by emphasizing some fundamental principles, so that the student will be better able to grasp and understand the general relationships governing physical properties and chemical reactions of organic compounds." This purpose is admirably achieved by the author. Concurrently, a problem of the student (as well as the instructor) is how to cope with the ever-expanding organic textbooks. This point is mentioned not as a particular criticism of the book under discussion but as a problem that accompanies almost all of the more recent organic textbooks.

From the standpoint of the instructor, organic texts can be classified into two categories: (1) those that present a minimum of material with full and detailed description such that the lecture time is given over primarily to supplementary material, and (2) those that present most of the desired material, the lecture periods being employed for the elucidation of the material covered. This

book belongs to the latter classification. Since many additions were necessary during the revision, a number of superfluous sentences have been efficiently eliminated from the first edition.

The order of presentation follows very closely that of the first edition, with separate treatment of aliphatic and aromatic chemistry. Chapters 2 and 3 (34 pages) discuss fundamental concepts such as energy relationships, resonance, dipole moments, ionic character in covalent bonds, and relative electronegativities; these concepts are then used in the subsequent portions of the book. Some attention is devoted to reaction mechanisms, though not sufficient to confuse the beginning student completely.

The cycloalkanes and the strain theory of rings are introduced early (Chapter 7). Organometallics are also discussed early and in a separate chapter, thus permitting their use throughout the remainder of the text. As with the first edition, the ethers, esters, anhydrides, and acyl halides are described simultaneously "in order to emphasize their similarities and differences." The final seven chapters include the usual more complex compounds as well as the amino acids, proteins, and carbohydrates. It would be difficult to include these topics in a one-year course while following the chapters chronologically.

One of the outstanding features of this work is the number and quality of the problems at the end of each chapter; these exercises should prove an invaluable aid to the beginning student.

The book appears to be well indexed and relatively free of errors. As might be expected, some inaccuracies have been overlooked. For example, on page 68 reference to Chapter 15 is given for the preparation of alkenes from bromoethers; this material, however, is found in Chapter 17. On page 85, sodium 2-butynoate is named sodium propiolate. On page 128, incorrect formulas are given for the dithiopropionate and ethanesulfinate ions.

The amount of material and the manner in which it is covered make this an excellent text for the better students. For students of lesser stature, portions of the book could be omitted; however, it is the opinion of the reviewer that extensive use of this method is not as desirable as would be the use of a less complete textbook with fewer omissions.

ROBERT K. INGHAM

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● FORMALDEHYDE

J. Frederic Walker, **Chemical Research Division, Electrochemicals Department, E. I. du Pont de Nemours & Co., Inc. Second edition. American Chemical Society Monograph Series. Reinhold Publishing Corp., New York, 1953. xvi + 575 pp. 41 figs. 59 tables. 16 × 23 cm. $12.**

RELATIVELY few individual organic compounds are sufficiently significant industrially and academically to warrant publication of an A. C. S. Monograph that is solely concerned with the chemistry of a specific molecule. Formaldehyde has long occupied a rather unique position in organic chemistry and in recent years its industrial importance has steadily increased. An expanded revision of the original A. C. S. Monograph No. 98 seems very much in order.

The major points of expansion in this second edition (A. C. S. Monograph No. 120) are the chapters on formaldehyde production; commercial formaldehyde solutions and the behavior of the substance in aqueous solution; its reactions with hydroxy compounds, amines, amides, heterocyclic compounds; and hydrocarbons and their derivatives. The chapters on hexamethylenetetramine and the uses of formaldehyde and its polymers have also been enlarged.

The discussions of the nature and behavior of aqueous solutions of formaldehyde are particularly interesting. There is some degree of repetition in the presentation of this material. Although the author notes that he had no intention of developing an exhaustive treatment of the chemistry of formaldehyde, a thorough examination of the book can be exhausting. The most significant reactions of the compound with the more conspicuous functional groups seem to be covered reasonably well. Occasional discussions of the structural aspects of certain molecules and reaction mechanisms may appear rather cursory. However, the obvious limitations of space and the inherent character of the book must be considered when criticizing the exposition. The number of references to the original literature is probably adequate for a book of this type.

The book is well written; the style is clear and polished. The author and subject indexes are quite adequate. Because this volume is the largest modern collection of material on formaldehyde, it should occupy a prominent position in our chemical literature.

DONALD C. GREGG

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● AN AMERICAN IN EUROPE: THE LIFE OF BENJAMIN THOMPSON, COUNT RUMFORD

Egon Larsen. **The Philosophical Library, New York, 1953. 224 pp. 4 figs. 28 plates. 14.5 × 22 cm. $4.75.**

FEW who relax before a well-constructed fireplace with a cup of drip coffee know the name of the man responsible for these improvements, or if they do know his name, they probably know little about his fantastic career. First a Tory spy, then an Under-Secretary in the office of the decrepit Lord Germain, and later minister of war and police in Bavaria (where he acquired his title), Benjamin Thompson's checkered political career was equaled by his erratic domestic adventures, which culminated in his marriage to Lavoisier's widow. Domestic science, the improvement of stoves and lamps, the concoction of soups, and the like, sounds like dull stuff, but Count Rumford, the founding father of this branch of the humanities, was not exactly a dull character, although sometimes an unpleasant one, and his contemporaries were lively in their reactions to him and his works. This biography is a readable account of an interesting and irascible personality, a genius of sorts and undeniably an ingenious inventor. Whether he should really be considered, with Jefferson and Franklin, as one of the three greatest minds we have produced, as F. D. Roosevelt once said, is a more debatable matter.

JOEL W. HEDGPETH

SCRIPPS INSTITUTION OF OCEANOGRAPHY
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● COMPREHENSIVE INORGANIC CHEMISTRY. VOLUME I

Edited by *M. Cannon Sneed,* Professor of Chemistry, *J. Lewis Maynard,* Professor of Chemistry, and *Robert C. Brasted,* Associate Professor of Chemistry, University of Minnesota. D. Van Nostrand Co., Inc., New York, 1953. xi + 232 pp. Illustrated. 15 × 23 cm. $5.

THIS volume is the first in a series of 11 that the editors introduce as "a reference work on the chemical elements and their inorganic compounds. . . comprehensive in the extensiveness of the fields covered rather than in the fullness of their treatment." "Emphasis has been placed largely on chemical properties and relationships and their interpretation in terms of theoretical concepts of atomic and molecular structure, the deductions from the periodic system, and the basic ideas relating to electrolytes." In view of this introduction and the material within this initial volume the reviewer wonders if the word *comprehensible* is not preferable to the title word *comprehensive.*

The first chapter, "Principles of atomic and molecular struc-

ture," by William N. Liscomb of the University of Minnesota, surveys chemical architecture mainly from the viewpoint of Pauling. Numerous applications of the principles of chemical binding to such substances as water, diborane, the oxides of nitrogen emphasize the ramifications of this approach. A brief treatment of the nature and properties of crystals as well as the structure of glasses and liquids completes this contribution.

"Theoretical and applied nuclear chemistry," by Paul R. O'Connor of the University of Minnesota, succinctly covers theoretical nuclear chemistry under the following five divisions: basic nuclear properties, fundamental properties, nuclear stability, spontaneous nuclear reactions, and preparation of isotopes. A minor disturbing feature is the presentation of the fundamental particles. The photon is not included. Further, the mesons are listed as a single group, whereas both the positive and negative electrons are presented. The application of stable and unstable nuclides to chemical problems is deftly treated. Among the topics considered are exchange reactions, ultramicrochemistry, and the use of tracers in analytical chemistry.

These two chapters are directed to the study of the 98 chemical elements. The first contribution is by Glenn T. Seaborg on "The actinide series" in the final chapter of this book. The subject is introduced with a general discussion of the electronic structures of these elements and their influence upon chemical and physical properties. The individual members are then presented: their isotopes, occurrence, chemical and physical properties, and uses.

The over-all presentation is remarkably uniform and coherent. Quite a high standard is set for the latter volumes. The principal usage of the set as a whole appears to be as a readily understandable reference for advanced courses in inorganic chemistry where a modern structural treatment is demanded. The first two chapters could well serve as the basis of a one-semester course for students unacquainted with quantum mechanics.

EDWARD D. GOLDBERG

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● SEMIMICRO QUALITATIVE ANALYSIS

Hervey Hubbard Barber, **Professor Emeritus of Chemistry, University of Minnesota, Professor of Chemistry, Lincoln Memorial University, and *T. Ivan Taylor,* Professor of Chemistry, Columbia University. Revised edition. Harper & Brothers, New York, 1953. xi + 404 pp. Illustrated. 15.5 × 24.5 cm. $4.50.**

THIS book is an extensive revision of a previous edition. It is intended for a fairly substantial course in semimicro qualitative analysis. A reasonably good background in general chemistry is desirable.

The first part of the book deals with cations and the second section with anions.

The arrangement of materials for each cation group is: preliminary experiments, summary of reactions in outline form, outline and discussion of procedure, theory of ionic equilibria applicable to the analysis, analysis of knowns and unknowns, chemical reactions in the analysis, questions, and problems.

Units and terms are well defined. Discussions are clear and in simple language. Much of the material is presented in table-outline form. There is some repetition of material but it does not necessarily detract from the worth of the book as a text.

In most cases where other good methods of separation are available they are given in the discussion. In connection with a discussion of the cation groups the authors include a good discussion of the behavior of the rarer elements with respect to these groups.

The general analytical scheme used is more or less standard. Group IIA is separated from group IIB with NaOH and CH_3CSNH_2. H_2S is replaced as a source of sulfide ion by CH_3CSNH_2 in both Group II and Group III.

Group III is divided into two sections. The first is divided into three parts and individual tests are run for Al^{+3}, CrO_4^{--}, and Zn^{++}. The second division is divided into four parts and individual tests are run for Fe^{+3}, Mn^{++}, Co^{++}, and Ni^{++}.

The anion analysis includes tests for 23 anions. The anions are discussed in an independent section in the back of the book and probably would be omitted in brief courses.

The methods of filtering and manipulating small amounts of material certainly warrant careful consideration by everyone interested in qualitative analysis.

RAY WOODRIFF

MONTANA STATE COLLEGE
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● THE SCREEN PROJECTION OF CHEMICAL EXPERIMENTS

E. J Hartung, **Professor of Chemistry, University of Melbourne. Melbourne University Press; New York: Cambridge University Press, 1953. xiv + 291 pp. 14 plates. 67 figs. 14.5 × 22.5 cm. $4.75.**

IN VIEW of our large lecture classes that seemingly get larger each year, the reviewer is happy to see collected in one place a handy reference to a fairly new and relatively undeveloped instructional tool. This book is designed for the chemistry teacher as an aid in setting up lecture demonstrations that can be projected onto a screen. Approximately 350 projection experiments are described and indexed, ranging from absorption spectra to wetting of glass and wax. The major fields in which projection demonstrations are presented include gases, liquids, solids, solubility, chemical reactions, diffusion, electrochemistry, surface chemistry, colloids, photochemistry, and color phenomena. Many of these are adaptations of conventional lecture demonstrations, but there is shown a considerable amount of ingenuity in adapting these to projection demonstrations. There are, as well, a number of new experiments which show considerable thought and planning in their development. A study of these experiments will almost certainly suggest new ones to the reader.

A general index refers to those sections of the book which deal with apparatus and equipment. Although the references to commercially available equipment are not specific, there is ample discussion to orient one to the types of equipment which are available. The author describes several pieces of gadgetry which can be constructed in the lecturer's workshop. The implication would leave the uninitiated with the impression that many of these items are unavailable commercially.

The book does not mention or allude to the more modern type of equipment which has been specially designed for vertical projection. In this respect the references imply a lack of acquaintance with the most recent developments in this area.

The physical make-up of the book is satisfactory. The binding is only fair but probably will be sufficient for the type of use to which it will be submitted. Any lecturer in chemistry or other physical sciences who wishes either to expand or improve his classroom demonstrations will profit by a study of this book.

W. H. SLABAUGH

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● THE ORIGIN OF LIFE

A. I. Oparin. **Translated by *Sergius Morgulis.* Second edition. Dover Publications, Inc., New York, 1953. xxiv + 270 pp. 13.5 × 20.5 cm. Paper bound. $1.70.**

THIS new edition is essentially the same as the 1938 edition with the addition of a new preface by the translator to remind the reader of some of the recent discoveries bearing on the problem of biochemical evolution and the nature of life.

• INORGANIC QUALITATIVE ANALYSIS: SEMI-MICRO TECHNIQUE WITH ESTIMATION OF CONCENTRATIONS

Harold A. Fales, Professor of Chemistry, Rutgers University, Newark Colleges, and *Frederic Kenny,* Assistant Professor of Chemistry, Hunter College, New York. Third edition. Appleton-Century-Crofts, Inc., New York, 1953. xii + 284 pages. 39 figs. 15 tables. 14.5 × 21.5 cm. $3.

THIS is the third edition of the book, which first appeared in 1943. It is intended for students who have had only two quarters or one semester of general chemistry, and can be adapted to either a year or a half-year course. It should also serve well for the laboratory part of a comprehensive course in the inorganic chemistry of the metals and nonmetals during the last part of the first year.

The book is divided into two sections. The first deals with theoretical material; the second deals with laboratory techniques and procedures. Fourteen supplementary experiments are included. They serve as a convenient abbreviated substitute for knowns. A few of the supplementary experiments are used to illustrate theoretical topics discussed in the first part of the book.

The authors attempt to correlate lecture and laboratory work but their attempt is only partly successful. It is difficult to correlate such topics as atomic structure, acids and bases, ionization, conductivity, and pH with the laboratory separation and identification of metals.

Very little is said about the general or inorganic chemistry of the ions studied in the laboratory. Equations are given for the analytical reactions used and some of the separations are briefly discussed.

The more or less standard analytical scheme is used. Sulfide ions are furnished by H_2S and centrifuges are used to separate precipitates. Cu^{++} and Cd^{++} are separated with powdered iron. Many instructors feel that KCN or $Na_2S_2O_4$ give somewhat better results.

The anion procedure provides for the identification of 12 anions. Standard tests are used, in general, but a scheme of analysis similar to cation analysis is set up rather than elimination tests and then individual tests for ions not eliminated.

The book is well written and easily understood, and should receive consideration from anyone looking for a text of this type.

RAY WOODRIFF

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• RADIATION CHEMISTRY

Discussions of the Faraday Society, No. 12. Aberdeen University Press, Ltd., Aberdeen, 1952. vii + 319 pp. Illustrated. 15.5 × 25 cm. 35*s*.

THIS book contains the technical papers presented at a General Discussion on Radiation Chemistry held by the Faraday Society at Leeds University in April, 1952. With respect to organization, the book is divided into four sections, each of which is concluded with a general discussion of the papers in the section.

In the first section, the papers deal with the primary act of absorption of ionizing radiation in condensed and in gaseous systems. The nature and reactions of the ions and "hot atoms" formed are discussed.

The papers in the second section are related to actinometry and the radiolysis of pure liquids. Included is a critical review of the chemical dosimetry of ionizing radiation, dosimetry measurements in a pile, and the radiation decomposition of water and pure organic liquids.

In the third section the papers are on the subject of the indirect action of ionizing radiation in aqueous systems containing a single solute. Water is such an important solvent in chemical and biological systems that aqueous solutions have always received a great deal of attention. Since irradiation of aqueous solutions leads to the formation of hydrogen peroxide as one of the important products, it is understandable that there are several papers in this section on the formation and decomposition of hydrogen peroxide. Attention is also given to the radiation chemistry of organic solutes and to the inactivation of bacteriophage.

The three papers in the last section are on the subject of protection and sensitization. Protection, *i. e.*, reduction of the radiation effect on one solute achieved by addition of a second solute, may be a very important effect in biological systems.

The book is more than an excellent status report of radiation chemistry; it is also a valuable and inspiring source of ideas for research in a field which is in its infancy and offers many exciting challenges to biologists, chemists, and physicists alike.

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• ADVANCES IN VIRUS RESEARCH. VOLUME I

Edited by *Kenneth M. Smith,* Virus Research Unit, Molteno Institute, Cambridge, England, and *Max A. Lauffer,* Department of Biophysics, University of Pittsburgh, Pittsburgh, Pennsylvania. Academic Press, Inc., New York, 1953. vii + 344 pp. Many figs. and tables. 16 × 23.5 cm. $8.

THE major objectives of this first volume of a new series of review articles devoted to general virology are clearly stated in the preface: "Virus research is carried out by individuals representing widely diversified specialties in the physical and in the biological sciences. . . . The natural result is that the findings in this area are published in a great number of journals reflecting the backgrounds of the individual investigators. . . . 'Advances in Virus Research' is planned to help surmount this obstacle encountered by those who attempt to follow virus literature."

In the reviewer's judgment, the objectives of the editors have been fully achieved, and the fact that they have chosen to emphasize the virus itself, rather than the disease it produces, is ample insurance that the high standards of the current volume will be maintained as new volumes appear at yearly intervals.

The great diversification of virus research is illustrated by the eight topics which appear in the first volume. The first article, by H. T. Epstein, an associate of one of the editors, discusses the viruses that afflict bacteria and considers 124 papers, most of which have appeared since 1945, and many of which date from 1950. Particular emphasis is placed on the biochemistry, genetics, and life cycle of bacteriophages. The second article, by C. W. Bennett, deals with the interactions between plant viruses and virus strains and discusses in some detail the various theories advanced to account for cross-protection phenomena exhibited by plant viruses. The third paper, "Transmission of plant viruses by cicadellids," is by L. M. Black, and considers the literature concerned with the transfer of plant viruses by leafhopper insects. In the fourth paper G. H. Bergold takes up the work on the 100 or so viruses that attack insects. The fifth paper, by Werner Henle, evaluates 158 papers that describe the reproductive behavior of flu virus. The paper is entitled "Multiplication of influenza virus in the entodermal cells of the allantois of the chick embryo." The sixth paper, "Poliomyelitis," by J. L. Melnick, covers 200 papers relating to the behavior of the virus responsible for infantile paralysis. The seventh paper, by D. G. Sharp, describes methods used in the purification of animal viruses and evaluates various criteria used to assess the purity of isolated animal viruses. The eighth paper is also by an associate of one of the editors. The title of Roy Markham's paper is "Virus nucleic acids" and represents a critical appraisal of current knowledge on the chemical composition, physical properties, and behavior of nucleic acids obtained from representative animal, plant, and bacterial viruses.

The publisher is to be congratulated for realizing the great need for the integration of the vast literature of virology and providing

a meeting place where the latest advances in virological research can be presented. The editors, too, deserve thanks for insisting that all branches of virology be represented with the focus of attention limited to the virus itself. Clearly, this series will become an indispensable aid to all those interested in general virological matters.

S. G. WILDMAN

UNIVERSITY OF CALIFORNIA
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● LABORATORY MANUAL FOR A SHORT COURSE IN ORGANIC CHEMISTRY

E. Campaigne, **Indiana University, and** ***Harold Hart*** **and** ***Robert D. Schuetz,*** **Michigan State College. Second edition. Houghton Mifflin Co., Boston, 1953. 153 pp. 11 figs. 20.5 × 27.5 cm. $2.50.**

THIS manual is intended for use in the one-semester or one-quarter course taught to majors in agriculture, nursing, home economics, etc. It includes 27 experiments, each designed to be completed in a three-hour laboratory period.

Of necessity such a manual must be slender, both in the amount of chemistry covered and in the depth of penetration into chemical phenomena. In the present case, the slenderizing has been done well, for the manual has a lightness of touch but at the same time a firm emphasis on fundamental chemical principles.

Besides many experiments of the test-tube variety, there are several novel small-scale preparative experiments, most of which involve reaction times of less than thirty minutes. These include a Grignard reaction run in an open test tube. Two experiments call for work with molecular models: Experiment 2 involves exploration of the geometrical character of organic molecules and of the relationships of three-dimensional models to two-dimensional structural formulas; Experiment 24 deals with stereoisomerism. Each experiment is followed by a perforated report sheet, with questions and blanks for answers.

This book should be seriously considered by every teacher of the sort of course for which it is intended.

JOSEPH F. BUNNETT

UNIVERSITY OF NORTH CAROLINA
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● ENGINEERS AS WRITERS: GROWTH OF A LITERATURE

Edited by ***Walter J. Miller*** **and** ***Leo E. A. Saidla,*** **Department of English, Polytechnic Institute of Brooklyn. D. Van Nostrand Co., Inc., New York, 1953. xii + 340 pp. 16 figs. 15 × 22.5 cm. $4.25.**

THIS is a most unusual—a unique—book. Maybe not actually discouraged, but frankly dissatisfied with the results of trying to teach students in engineering how to write by cramming them full of grammatical rules and mechanical Do's and Don't's, these teachers of English in the Polytechnic Institute of Brooklyn decided to follow the example of their teaching brethren in their own field. Inspired by the methods used and the sources available in analogous study of other forms of writing, *e. g.*, poetry, drama, journalism, the authors have assembled a splendid collection of writings by eminent engineers, each skilled in his own branch.

Ever since Aydelotte's "English and Engineering" (McGraw-Hill, 1923) was allowed to go out of print, there has been a gap in the lists of literary offerings to technical students. Whereas the older "reader" aimed to teach by precept and by example, this new one concentrates on examples, confident that students will be able to derive the precepts from them.

It is well subtitled "Growth of a Literature." Following an interesting introductory chapter on the historical development of writing by engineers from the earliest times, are thirteen chapters, each limited to an authoritative piece of writing. The first three—Vitruvius on architecture (27 B.C.), Frontinus on aqueducts, Agricola on mining—are in the best available translations from the original Latin. Others represented are Smeaton on his lighthouse, McAdam on road-building, Rankine of the model manuals, Wellington on railways; and, nearer our own time, Lamme on electric power, Parsons on steam power, Taylor on scientific management, Pupin, Ammann, Hoover, Benedict and Rubin, and finally, Raymond's classic, "The Well-Tempered Aircraft" (1951).

An enormous amount of research and thoughtful planning have gone into this book. The well chosen selections make widely varied reading: some interesting—occasionally fascinating—some aridly factual, some boring. Each is preceded by a short sketch about the author, his work, and the background of the piece that follows. At the end of each chapter the reader is jerked back by the authors' comments on why the piece is good, what is the matter with it and why, and their suggestions for further study of each topic.

Come to the epilogue, the student or other reader is given suggestions for appraising the book. One cannot fail to note that it has given examples of almost every form of composition that may be demanded of engineers: letters, formal and informal reports, discussional and expository papers, addresses to technical and nontechnical audiences, manuals of instruction. Anyone who tries to make the critical evaluation as outlined can easily understand why some of the selections make a stronger appeal than others.

The book is well made. It has an excellent bibliography, an adequate index, and a helpful table inside the back cover for the speedy locating of certain topics. Any teacher of either technical subjects or technical writing should find it most valuable. And any student that uses it in school will probably be tempted to annotate it with his own comments and keep it for ready reference during his professional career.

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● THE HANDBOOK OF SOLVENTS

Leopold Scheflan, **Technical Manager, B. Scheflan, Ltd., and** ***Morris B. Jacobs,*** **Director of Laboratory, Department of Air Pollution Control, New York City. D. Van Nostrand Co., Inc., 1953. viii + 728 pp. 17 figs. 17 × 25 cm. $10.**

AN INTRODUCTORY section of 78 pages discusses the classification of solvents, their safe handling, solvent power, vapor pressure, dilution ratios, flammability limits, and recovery by absorption and adsorption methods.

Tabulated data are given for 2740 organic solvents, mostly pure compounds, but commercial solvents are also included. Up to 28 physical properties are listed for well-known compounds.

An index of synonyms enables the user to go from commercial to scientific names.

● DISTILLATION LITERATURE: INDEX AND ABSTRACTS, 1946–52, INCLUSIVE

Arthur Rose **and** ***Elizabeth Rose,*** **Applied Science Laboratories, Inc., and Pennsylvania State University, State College, Pennsylvania. Applied Science Laboratories, Inc., 1953. 600 pp. 18.5 × 26 cm. $25.**

A COMPLETE index and abstracts of the literature on distillation for the years 1946 to 1952 (a previous volume covered 1941 to 1945). A condensed list of subject index headings is followed by the abstracts arranged according to this index. There is an author index. Patents are included.

Out of the Editor's Basket

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mmer Course for Secondary School achers

A new course on "Current Develop-nts in Science" for secondary-school ence teachers will be offered by the rvard Summer School this year. It l be taught by Professor Eugene G. chow, member of the Harvard Chem-y Department and pioneer in silicone emistry. A number of special fellow-ships are available for the course, which continues the series in Science Education initiated by former President James B. Conant of Harvard.

Further information about this course and about the fellowships can be obtained from the Harvard Summer School, 2-L Weld Hall, Cambridge 38, Massachusetts.

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The Micro-Viewscope combines in one unit a microscope with 75X and 500X magnification with enclosed illuminating and projection elements that render a brilliant image on an 8-in. ground glass screen on a sloping desk. A mechanical stage gives precision control for centering or scanning details of a slide; and the unit is also equipped for photomicrography.

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Union Carbide Scholarships

New allocations of Union Carbide Scholarships to become effective in the fall of 1954 will bring the number of scholarships at present allocated to a total of 308 of a proposed goal of 400. Ten more educational institutions recently

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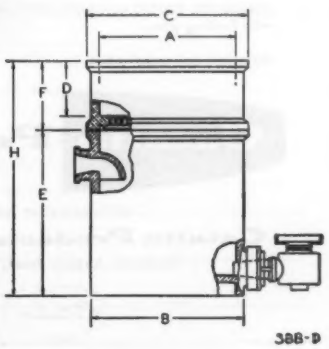

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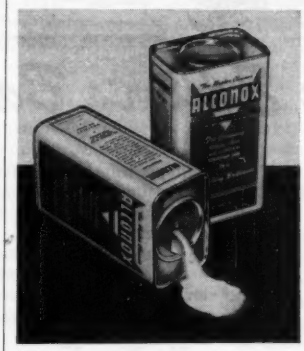

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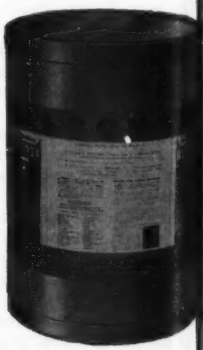

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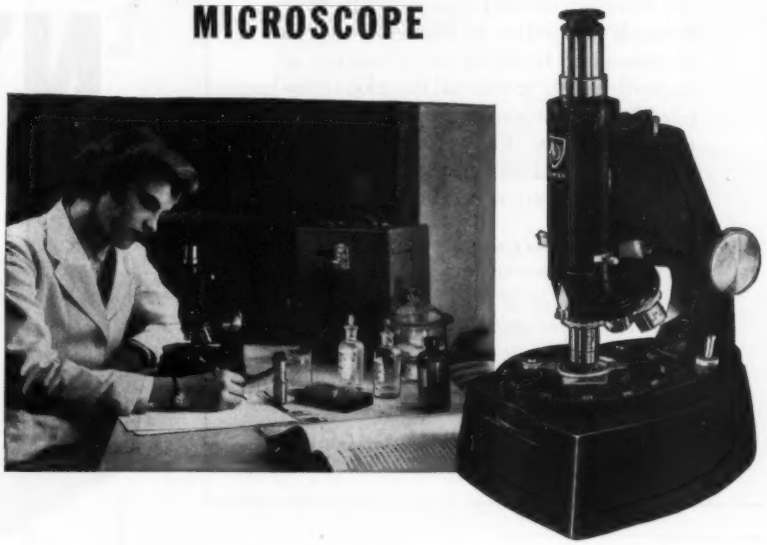

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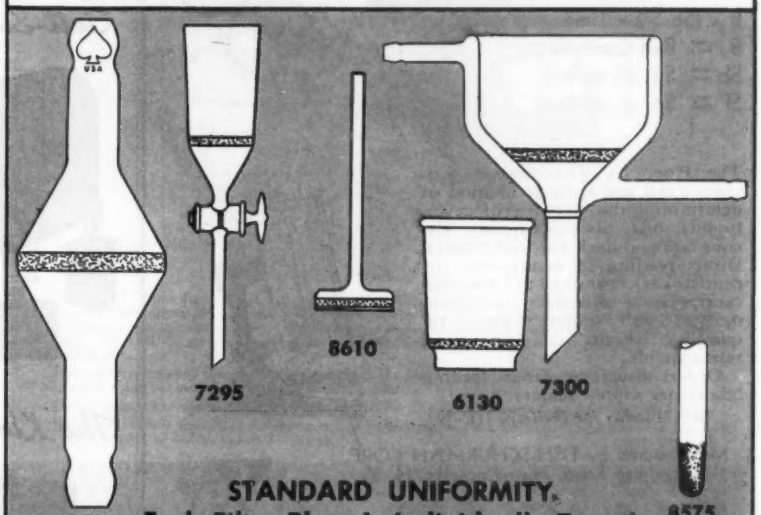

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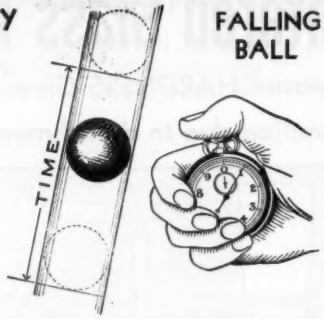

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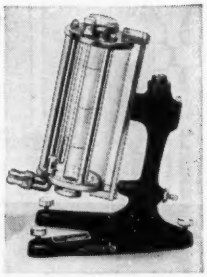

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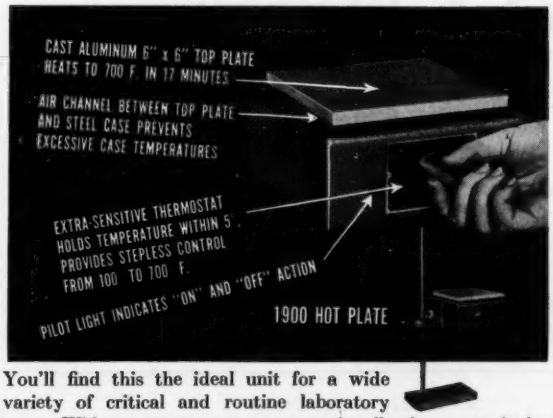
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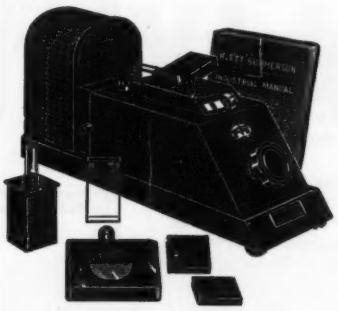

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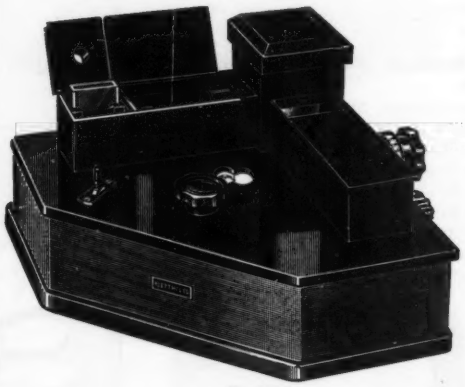

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nounces spring courses dealing with industrial and economic chemistry. Their brochure states that their objective is to give a sketch of the general problem represented by their national industrial economy, pointing out the different fields possible for those interested in careers in chemistry. The courses are not exclusively for professional chemists or students. Information on the program may be obtained from the Secretary of the Faculty, Ing. Fco. Garibi Velasco, Universidad Autónoma de Guadalajara, Guadalajara, Jal., Mexico.

Fire Prevention

A pamphlet on "Fire Prevention for Secondary Schools: Materials and Methods for Fire Prevention Education Within High School Subjects" has been prepared in a curriculum workshop at the University of Southern California in the summer of 1951. The objective of the workshop was to produce this publication.

The venture had the complete backing of the local Fire Service and the local insurance companies, as well as the International Association of Fire Chiefs, which adopted and published the completed book.

The book attempts to bring to the attention of each subject-matter teacher those areas and activities which he might perform and which have a definite bearing on problems of fire prevention.

Copies of this publication may be obtained by writing to the International Association of Fire Chiefs, Inc., Martinique Hotel, New York 1, N. Y. Cost of the book is $1.50.

Atlas Powder Company Scholarships

Atlas Powder Co. has set up eight $1000 college scholarships for science students. The grants are part of the company's program to enable outstanding students to complete their scientific education in order to help meet some of industry's pressing needs for technical personnel.

The awards will go to students who will be seniors during the 1954–55 college year, majoring in chemistry, physics, or any branch of engineering. The program, initially being proposed to 40 colleges and universities, will be administered by the Atlas committee on scholarships.

Scholarships will be awarded on the basis of scholastic records and the recommendations of the college staff. Extracurricular activities and financial need also will be factors. The grants will be used to pay tuition, board, travel, and other senior-year costs, as approved by the institution. Further information may be obtained from Atlas Powder Co., Wilmington 99, Del.

New Literature

● A new catalogue of educational laboratory equipment has just been issued by Metalab Equipment Corp. It contains extensive information on Combination Science Desks, Center Tables, Instructors' Desks, and Homemaking Units designed for the modern school laboratory.

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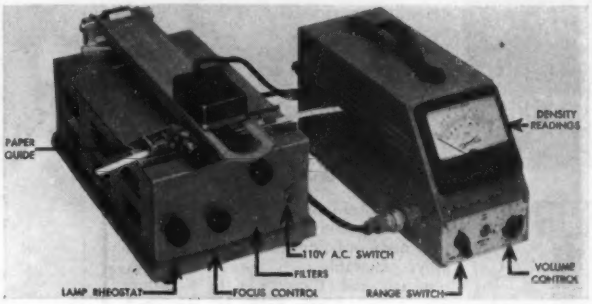

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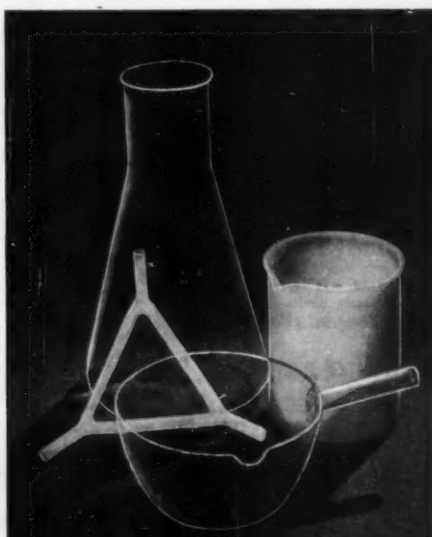

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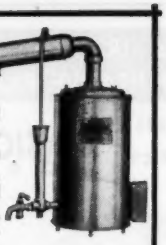

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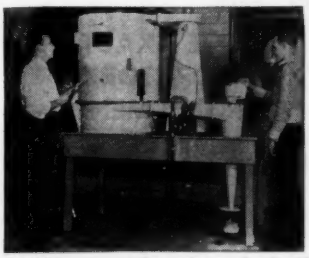

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● A thirty-two page manual has been compiled by the engineering staff of E. H. Sargent & Co., to serve as a review of fundamental theory of operation and response mechanism in the field of oscillometry, and to provide a working basis for measurements in this field and their interpretation. Special emphasis is placed on the Sargent Model V Oscillometer. The manual contains sections on the theory and characteristics of the method, technique, operational procedures, laboratory exercises and reference data. The price per copy is $2.00. An educational quantity discount is available to institutions offering instrumentation courses and research in oscillometry. Further information is available from E. H. Sargent & Co., 4647 W. Foster Avenue, Chicago 30, Illinois.

● Its standard line of agitated kettles is the feature of a new brochure just issued by The Colonial Iron Works Co., 17643 St. Clair Ave., Cleveland 10, Ohio. Kettles are available in metals ranging from aluminum to stainless steel. They are available in all pressure ratings based on fixed outside shell diameters in code and noncode construction. Among the units discussed are autoclaves, hydrogenators, mixers, neutralizers, polymerizers, reactors, sulfonators, and other standard and custom-made products.

● A new 12-page bulletin describing the DuMont Type 323 wide-band Cathode-Ray Oscillograph has just been published by the Instrument Division of Allen B. DuMont Laboratories, Inc. The new booklet gives complete specifications about the instrument and contains illustrations of the instrument and circuit diagrams. It is available upon request from the Technical Sales Dept., Allen B. DuMont Laboratories, Inc., 760 Bloomfield Av., Clifton, New Jersey.

● Central Scientific Co. has issued its new 1954 Lab Listing which contains 400 new items of scientific instruments and laboratory apparatus that have been added to the Cenco listing since the publication of the company's General Catalogue J-150. The booklet, a 64-page supplement to the General Catalogue, presents photographs and descriptions of the new apparatus as well as a current price list. Copies can be obtained by writing to Central Scientific Co., 1700 W. Irving Park Rd., Chicago 13, Illinois.

● Schaar & Co. offers a new 8-page catalogue devoted exclusively to laboratory items made of Polyethylene. Included are many items not previously fabricated in Polyethylene. Available on request from Schaar & Co., 754 W. Lexington St., Chicago 7, Illinois.

● Fisher Scientific Company announces publication of the new edition of the

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"In speaking of apparatus, Dr. Müller makes a point which, in our opinion, has not been sufficiently emphasized previously in spite of a considerable mention of it in the literature; very satisfactory polarographic analysis may be performed with a most simple apparatus . . . . . Clarification of this point should serve to expand the teaching and application of polarography. For those interested in familiarizing themselves with the method, we recommend, "The Polarographic Method of Analysis' as an excellent starting point."

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The new Index can double as a manual of essential information, since it gives structural formulas, molecular weights, melting points, and boiling points for most of the chemicals, and color index numbers for dyes and stains.

The Index is catalogue number 115-C, and is available without charge from Fisher Scientific Co., 717 Forbes St., Pittsburgh 19, Pa.

● A new Office of Education publication is "A Directory of 2660 16 mm. Film Libraries," by Seerley Reid and Anita Carpenter, Office of Education Bulletin 1953, No. 7. It is offered for sale by the Superintendent of Documents, U. S. Government Printing Office, Washington 25, D. C., for 50 cents.

This directory is a state-by-state and city-by-city list of sources from which 16-mm. films can be borrowed or rented. It includes libraries which handle entertainment films and those which handle instructional films, and lists libraries having from one to thousands of films. It includes, also, commercial dealers, colleges and universities, city and state school systems, public libraries, industrial companies and trade associations, labor unions, civic groups, religious institutions, and Government agencies.

This publication will be helpful to teachers, school administrators, librarians, community leaders, and others who use or may wish to use motion pictures in their educational and informational programs.

● "Columbia Research News in Engineering and Science, 1954 Annual," is now available. It is a compilation of material taken from *Columbia Research News*, the news letter of developments in the science and engineering departments of Columbia University. This booklet describes, in an informal way, some of the activities and researches of the various segments of Columbia University having to do with science and engineering. Inquiries concerning this pamphlet should be addressed to Columbia Research News, Columbia University Engineering Center, 4 West 43rd St., New York 36, N. Y.

● A new brochure on Aritemp resins is available from Aries Laboratories, Inc., 270 Park Ave., New York 17, N. Y. This bulletin describes the use of Aritemp casting resins for the encapsulation and embedment of electronic components and circuit assemblies.

● "Visual-arc Spectroscopic Analysis," by Maurice J. Peterson and Howard W. Jaffe, Bureau of Mines Bulletin 524, is now available for 75 cents from the Superintendent of Documents, U. S. Government Printing Office, Washington 25, D. C.

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6	13/16	5/8	3 1/4"	1.40	14.00
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New Sealed Accessories

FOR CENTRIFUGING INFECTIOUS MATERIALS

Purpose

Laboratory administrators interested in the health of their laboratory personnel have recently become concerned with infectious aerosols sometimes encountered during centrifuging. Infectious materials sealed in centrifuge tubes or bottles quickly become airborne when they are released by a leak or fracture of the container due to high centrifugal forces. The natural draft created by the fan action of the rotating head acts to distribute the material through the laboratory.

Approach

International Equipment Company engineers have adapted standard accessories to permit sealing of the centrifuge cup. To insure maximum safety, the scientist having completed centrifuging removes the sealed container to a hood for opening. In those instances where a leak or fracture has allowed the material to contaminate the container, immediate decontamination steps may be taken.

Solution

A series of accessories based upon the Hi-speed 250 ml. slotted cup has been designed. The standard cup is threaded to take a dome cover fitted with an O-ring seal. The cup holds one of the standard round or flat bottom 250 ml. centrifuge bottles. Adapters are available for holding: 2–50 ml. centrifuge tubes; 7–15 ml. centrifuge tubes; and 10–13 x 100 mm. serum tubes.

Centrifuge	Head	No. Cups	R.P.M.	R.C.F.
Size 1, Model SBV	277	4	3000	2000
Size 2, Model V...	277	4	2900	1880
Size 2, Model V...	266	6	2300	1410
Model PR-1.....	284	4	2400	1240

2734 — Duralumin Cup, 250 ml., with screw dome cover and gasket, including 582 rubber cushion — $36.00.

2738 — Wrench, spanner type for tightening screw dome on 2734 — $1.75.

2741 989 2740

2741 — Adapter, 2-place, for 50 ml. centrifuge tubes, fits 2734 or any standard IEC 250 ml. centrifuge cup — $4.50.

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